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| <p>(21) International Application Number: PCT/US91/03118</p> <p>(22) International Filing Date: 10 May 1991 (10.05.91)</p> <p>(30) Priority data: 524,738 17 May 1990 (17.05.90) US</p> <p>(60) Parent Application or Grant (63) Related by Continuation US 524,738 (CIP) Filed on 17 May 1990 (17.05.90)</p> <p>(71) Applicants (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). UNIVERSITY OF SOUTH CAROLINA [US/US]; Osborne Administration Building, Columbia, SC 29208 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : CHAPMAN, James, Mood [US/US]; 1111 Watermark Place, Columbia, SC 29210 (US). KOLLMAYER, Willy, Dietrich [US/US]; 28 Raphael Road, Hockessin, DE 19707 (US). KOSH, Joseph, William [US/US]; 105 Nut Tree Court, Lexington, SC 29072 (US). McCANN, Stephen Frederick [US/US]; 2012 Christiana Meadows, Bear, DE 19702 (US). SOWELL, Joseph, Walter [US/US]; 1704 Blackbird Drive, West Columbia, SC 29169 (US). ZWICK, Faith, Bleresch [US/US]; 1228 Paper Mill Road, Newark, DE 19711 (US).</p> | | <p>(74) Agents: COSTELLO, James, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US.</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> |
| <p>(54) Title: ARTHROPODICIDAL NITROETHYLENES AND NITROGUANIDINES</p> <div style="text-align: center; margin: 20px 0;"> $\begin{array}{c} \text{Z} \\ \parallel \\ \text{R}^1\text{-X-A-N} \quad \text{N-R}^3 \\ \quad \quad \\ \text{R}^2 \quad \quad \text{R}^4 \end{array}$ </div> <p style="text-align: right; margin-right: 50px;">(I)</p> | | |
| <p>(57) Abstract</p> <p>Arthropods are controlled in agronomic and nonagronomic environments by contacting them or their environment with an effective amount of a compound of formula (I), wherein R¹ to R⁴, X, A, and Z are as defined in the text, including arthropodicidal compositions containing said compound(s).</p> | | |

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TITLE

ARTHROPODICIDAL NITROETHYLENES AND NITROGUANIDINES

BACKGROUND OF THE INVENTIONField of the Invention

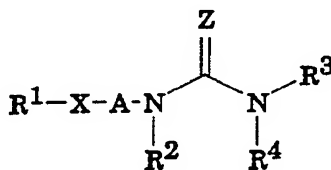
This invention concerns nitroethylene and nitroguanidine compositions and a method for using the nitroethylene and nitroguanidine compounds of Formula I to control arthropods in agronomic and nonagronomic environments.

State of the Art

Insecticidal nitroethylene compounds are disclosed in EPA 302,389 and EPA 302,833. Insecticidal alkylenediamines are disclosed in U.S. 4,025,529 and U.S. 4,806,553. Heterocyclic alkylenediamine insecticides are disclosed in EPA 254,859. Insecticidal 1-nitro-2,2-diaminoethylenes are disclosed in AU 88/20510. U.K. 1,483,633 discloses 2-(nitromethylene)-1,3-diazocycloalkanes as insecticides.

SUMMARY OF THE INVENTION

The invention pertains to use of compounds of Formula I, including all geometric and stereoisomers, agriculturally suitable salts thereof, and agricultural compositions containing them, for the control of planthoppers and leafhoppers. The compounds are:



I

wherein:

Z is selected from the group CHNO_2 and NNO_2 ;

X is selected from S(O)_n ;

A is selected from the group C₁-C₄ alkylene optionally substituted with C₁-C₃ alkyl, C₂-C₃ alkoxycarbonyl, halogen and CN;

5 R¹ is selected from the group C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₃-C₆ cycloalkyl and C₄-C₆ cycloalkylalkyl;

n is 0, 1 or 2;

10 R² and R³ are independently selected from the group H, CH₂CN, C₁-C₄ alkyl, CHO, C₂-C₄ alkylcarbonyl, C₂-C₃ alkoxycarbonyl C₂-C₄ alkoxyalkyl, C₃-C₆ dialkoxyalkyl, C₁-C₃ alkoxy, C₁-C₃ alkylsulfonyl, C₃-C₄ alkenyl, C₃-C₄ alkynyl, C₁-C₄ alkylamino, C₂-C₄ dialkylamino and benzyl substituted with R⁵;

15 R⁴ is selected from the group C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₃-C₆ cycloalkyl and C₄-C₆ cycloalkylalkyl; or

R² and R⁴ can be taken together as C₂-C₃ alkylene or C₂-C₃ alkenylene each optionally substituted with 1-4 C₁-C₂ alkyl; and

20 R⁵ is selected from the group halogen, C₁-C₂ alkyl, C₁-C₂ haloalkyl, C₁-C₂ alkoxy, C₁-C₂ thioalkyl, C₁-C₂ halothioalkyl, C₁-C₂ haloalkoxy, NO₂ and CN.

25 Preferred Method A for controlling plant and leaf hoppers comprises use of compounds of Formula I wherein Z is CHNO₂.

Preferred Method B employs compounds of Formula I wherein Z is NNO₂. Preferred Method C employs compounds A wherein:

A is CH₂CH₂;

R¹ is selected from the group C₁-C₄ alkyl;

30 R² and R³ are independently selected from the group H, C₁-C₄ alkyl, C₂-C₃ alkoxycarbonyl and C₂-C₄ alkylcarbonyl; and

R⁴ is selected from the group C₁-C₄ alkyl.

35

Preferred Method D employs compounds A wherein:

R² and R⁴ are taken together and independently selected from the group C₂-C₃ alkylene and C₂-C₃ alkenylene, each optionally substituted by 1-4 C₁-C₄ alkyl.

5

Preferred Method E employs compounds C wherein X is S.

Preferred Method F employs compounds D wherein X is S.

This invention also concerns novel arthropodicidal compositions comprising an effective amount of a compound of Formula I and a carrier therefor which is effective to deliver the compound to agronomic and nonagronomic arthropods, particularly planthoppers and leafhoppers, and their environment so that said arthropods are controlled.

In the above definitions, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl", denotes straight chain or branched alkyl such as methyl, ethyl, n-propyl, isopropyl or the different butyl isomers. Alkoxy denotes methoxy, ethoxy, n-propyloxy and isopropyloxy. Alkenyl denotes straight chain or branched alkenes such as vinyl, 1-propenyl, 2-propenyl, 3-propenyl and the different butenyl isomers. Alkynyl denotes straight or branched alkynes such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl isomers. Alkylthio denotes methylthio, ethylthio and the different propylthio and butylthio isomers. Alkylsulfonyl and alkylamino are defined analogously to the above examples. Cycloalkyl denotes cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

The term "halogen", either alone or in compound words as "haloalkyl", denotes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl" said alkyl can be partially or fully substituted with halogen atoms, which can be the same or different. Examples of haloalkyl include CH₂CHF₂, CF₂CF₃ and CH₂CHFCl.

The total number of carbon atoms in a substituent group is indicated by the "C_i-C_j" prefix where i and j are numbers from 1 to 6. For example, C₁-C₃ alkylsulfonyl designates methylsulfonyl through propylsulfonyl; C₂ alkoxy designates OCH₂CH₃ and C₃ alkoxy designates OCH₂CH₂CH₃ and OCH(CH₃)₂; C₂ alkylcarbonyl designates

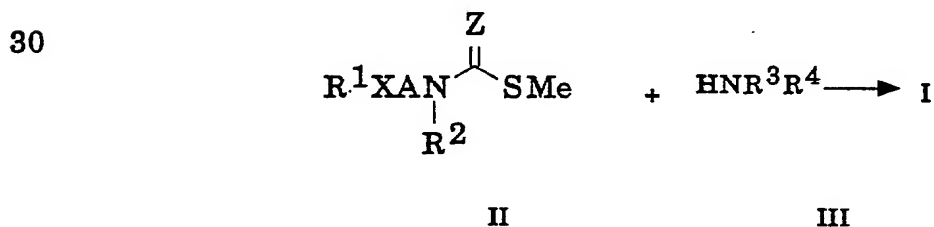
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C(O)CH₃ and C₄ alkylcarbonyl designates C(O)CH₂CH₂CH₃ and C(O)CH(CH₃)₂; C₃ alkoxyalkyl designates CH₂OCH₂CH₃ and CH₂CH₂OCH₃; C₄ alkoxyalkyl designates CH₂OCH₂CH₂CH₃,
5 CH₂CH₂OCH₂CH₃ and CH₂OCH(CH₃)₂; and as a final example, C₄ dialkoxyalkyl designates CH₂OCH₂CH₂OCH₃.

DETAILS OF THE INVENTION

The compounds of Formula I can be prepared by the reaction of nitroethenes and nitroimines of Formula II with an amine of Formula III (Scheme 1). Alternatively, compounds of Formula I can be prepared by the reaction of nitroethenes and nitroimines of Formula IV with amines of Formula V (Scheme 2) using procedures which are analogous to those used for reactions of compounds of Formula II with compounds of Formula III; therefore, for brevity only reactions of compounds of Formula II with compounds of Formula III are described. Typical conditions involve combination of II with a stoichiometric excess of III in a suitable solvent or combination of solvents at temperatures generally in the range of about 0 to 100°C. Suitable solvents typically have sufficient polarity to effect solution of the Formula II compound and the Formula III amine and include, but are not limited to, alcohols such as methanol, ethanol and isopropanol; ethers such as diethyl ether, tetrahydrofuran and dioxane; esters such as ethyl acetate; water; and polar and aprotic solvents such as dimethylformamide and dimethylacetamide. Amine III can also be used as its hydrochloride salt and in these cases an equivalent amount of a base (such as potassium hydroxide) is added to the reaction mixture.

SCHEME 1

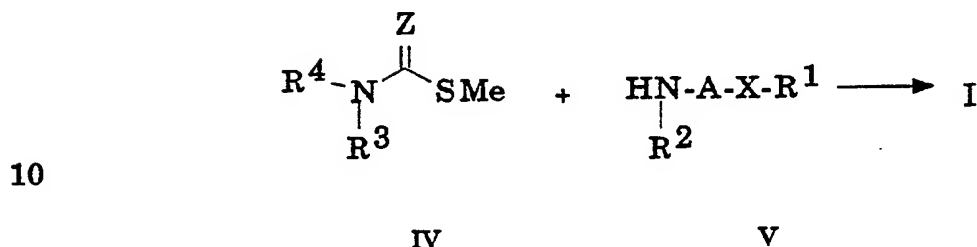


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wherein:

A, X, Z, R^1, R^2, R^3 , and R^4 are as previously defined.

SCHEME 2



wherein:

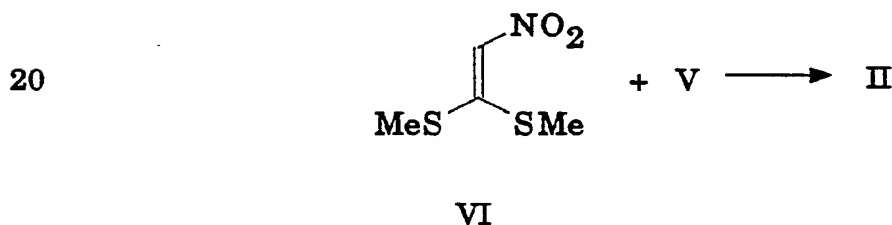
A, X, Z, R^1, R^2, R^3 , and R^4 are as previously defined.

Compounds of Formula I include both geometrical and optical isomers as well as Z and E isomers around the nitroethene or imine double bond. These isomers may vary in their biological activity. In some instances, it may be desirable to obtain compounds which are geometrically and/or optically pure or which are enriched in one or more of the possible isomers. All such isomers are included within the scope of the invention. They, as well as all salts, are included within the term "compound(s)".

For the sake of simplifying the description of this invention, the generic formula (Formula I) encompasses certain compounds that may have long term stability problems and/or are difficult to prepare. For example, haloalkylamines when R⁴ is C₁ to C₄ haloalkyl are unstable when the halo substituent is directly adjacent to nitrogen. These generally decompose to the corresponding hydrogen halides and imine. Similarly, Formula I compounds where A is a C₁ haloalkyl would be expected to be hydrolytically unstable. These compounds, however, are relatively few; their identity would be obvious to one skilled in the art, and their excision from the scope would unduly complicate and lengthen the description of the invention.

Compounds of Formula II where Z is CHNO_2 can be prepared using processes known in the art involving reaction of nitroethene VI with an amine of Formula V (Scheme 3). Compounds of Formula IV where Z is CHNO_2 can be prepared by procedures which are analogous to those for compounds of Formula II; therefore, for brevity, only the compounds of Formula II are described. Typical conditions involve the combination of equimolar amounts of V and VI in a suitable solvent or solvent mixture at temperatures in the range of about 0 to 100°C . Suitable solvents typically have sufficient polarity to effect solution of V and VI and include, but are not limited to, alcohols such as methanol, ethanol and isopropanol; ethers such as diethyl ether, tetrahydrofuran and dioxane; esters such as ethyl acetate; polar aprotic solvents such as dimethylformamide and dimethylacetamide; water as well as mixtures of solvents.

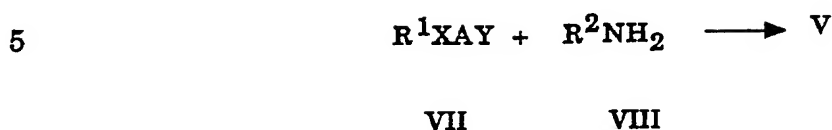
SCHEME 3



25 Amines of Formula V can be prepared by reaction of an alkylating agent of Formula VII with an amine of Formula VIII (Scheme 4). Typical conditions involve combination of VII with a stoichiometric excess of VIII in a suitable solvent or combination of solvents at temperatures in the range of about 0 to 100°C . Suitable solvents or solvent mixtures typically have sufficient polarity to effect solution of the Formula VIII amine and the Formula V product and include, but are not limited to, alcohols such as methanol, ethanol and isopropanol; ethers such as tetrahydrofuran and dioxane; water and acetonitrile. Amine VIII can also be used as its hydrochloride salt and in these cases an equivalent amount of a base (such as potassium hydroxide) is added to the reaction mixture.

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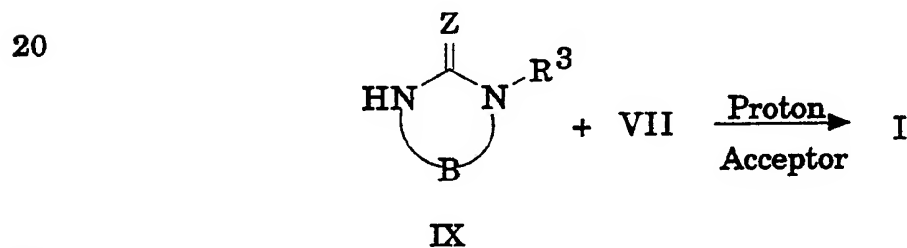
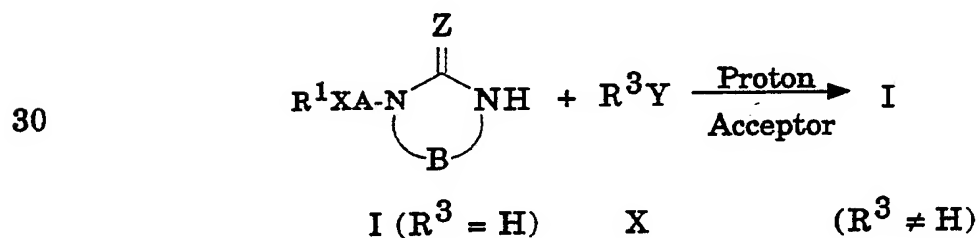
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SCHEME 4

wherein:

Y is a leaving group; and
A, X, R¹ and R² are as previously defined.

Compounds of Formula I where R² and R⁴ are taken together as an optionally substituted C₂-C₃ alkylene or C₂-C₃ alkenylene group can be prepared using the analogous procedures illustrated by Schemes 5 and 6.

SCHEME 5SCHEME 6

wherein:

B is C₂-C₃ alkylene or C₂-C₃ alkenylene each optionally substituted with 1-4 C₁-C₂ alkyl;

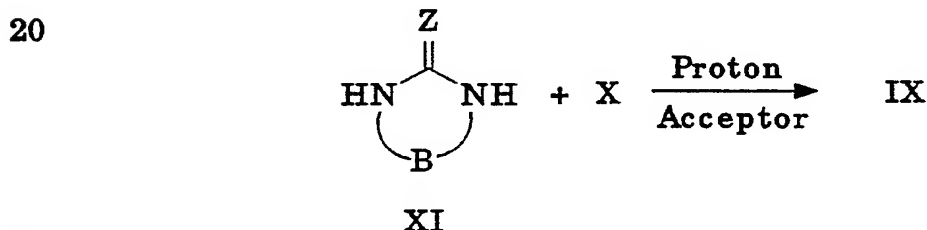
Y is a leaving group; and

5 A, X, R₁, R₃, and Z are as previously defined.

Reactions such as those shown in Scheme 5 are typically carried out by treatment of a solution of Formula IX and VII compounds in a suitable solvent with a proton acceptor such as, but not limited to, sodium hydride at a temperature of about 0 to 100°C. Suitable solvents include, but are not limited to, dimethylformamide and THF. Completely analogous procedures can be used to effect the reactions illustrated by Scheme 6, and, for the sake of brevity, will not be discussed further.

Scheme 7 illustrates the formation of Formula IX compounds. Procedures for this transformation are analogous to those previously described for Scheme 5.

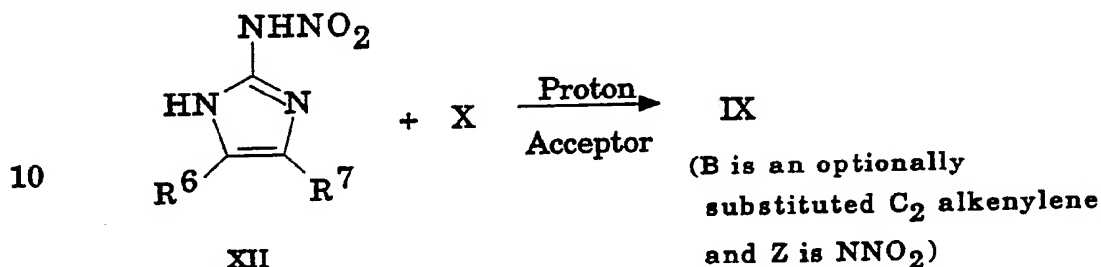
SCHEME 7



When B is equal to C₂ alkenylene and Z is equal to NNO₂, Formula XI compounds may exist as the amino-imidazole tautomer, XII. Scheme 8 illustrates the formation of Formula IX nitroguanidines using the precursors of Formula XII. Scheme 9 illustrates the formation of Formula I compounds where Z is NNO₂ and B is an optionally substituted C₂ alkenylene using the precursors of Formula XII. The

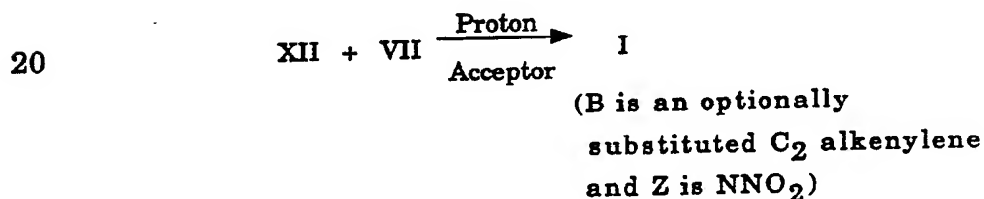
procedures illustrated by Schemes 8 and 9 are completely analogous to those described previously for Scheme 5.

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SCHEME 8

wherein:

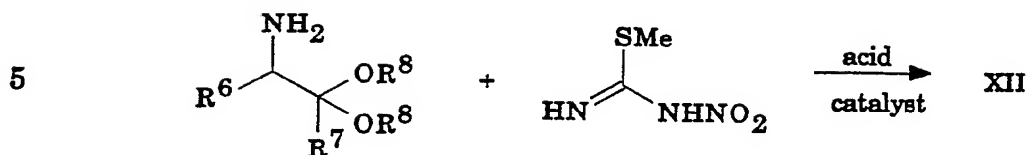
15 R⁶ and R⁷ are H, or C₁-C₂ alkyl.

SCHEME 9

25 Formula XII nitroaminoimidazoles can be formed by the reaction of S-methyl-N-nitro-isothiourea with amino-acetals of Formula XIII. Typical reaction conditions involve the treatment of a mixture of XIII and S-methyl-N-nitroisothiourea in a suitable solvent with 0 to 5 equivalents of an acid catalyst such as hydrochloric acid at a temperature of 0°C to

30 the reflux temperature of the solvent. Typical solvents include, but are not limited to, methanol, ethanol and isopropanol. Scheme 10 illustrates this transformation.

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SCHEME 10

XIII

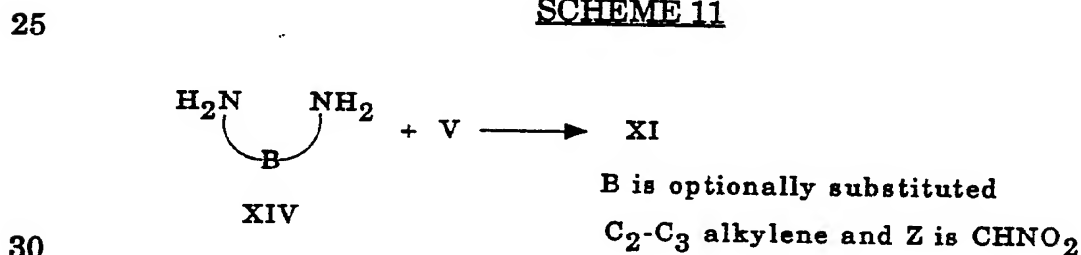
10 wherein: R^8 is an alkyl or aryl group; and
 R^6 and R^7 are as previously defined.

One skilled in the art will recognize Formula XIII compounds as acetals of α -amino aldehydes and α -amino-ketones, whose syntheses are well

15 preceded.

Compounds of Formula XI where B is an optionally substituted $\text{C}_2\text{-C}_3$ alkylene and Z is CHNO_2 can be prepared by the reactions of diamines of Formula XIV with V in a suitable solvent at temperatures in the range of about 0 to 100°C . Suitable solvents include, but are not

20 limited to, alcohols such as methanol, ethanol and isopropanol, and water, as well as other polar solvents. Typical reactions involve the use of equimolar amounts of V and XIV. Scheme 11 illustrates this transformation.

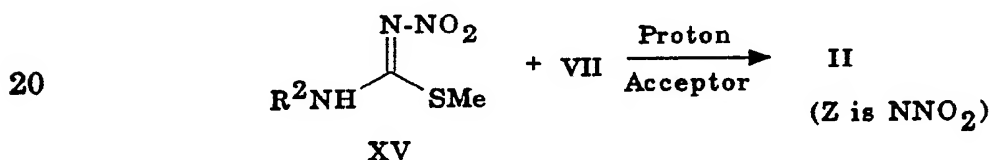
SCHEME 11

35 Compounds of Formula XI where B is an optionally substituted $\text{C}_2\text{-C}_3$ alkylene and Z is NNO_2 can be prepared by the reactions of Formula XIV diamines with nitroguanidine using procedures completely analogous to those described for Scheme 11 and, for the sake of brevity, will not be discussed further.

Formula XIV compounds are 1,2- and 1,3-diamines whose preparations are known in the art.

Compounds of Formula II where Z is NNO_2 can be prepared by the reaction of N-nitroimines of Formula XV with an alkylating agent of Formula VII in a suitable solvent in the presence of a proton acceptor (Scheme 12). Typical proton acceptors are metal hydrides such as sodium hydride, metal alkoxides such as sodium methoxide or potassium t-butoxide and carbonates such as cesium carbonate. Suitable solvents for reactions using metal hydride include DMF and THF. Suitable solvents for reactions using metal alkoxides include alcohols such as methanol, ethanol and t-butanol and THF. Suitable solvents for reactions using carbonate bases include methanol, ethanol and acetonitrile. The reactions are typically run at temperatures that range from 0 to 100°C . Typical reactions involve the use of equimolar amounts of VII and XV.

SCHEME 12



wherein:

25 R^2 is as previously defined.

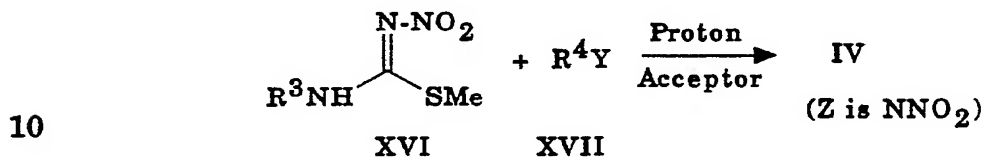
Compounds of Formula IV where Z is NNO_2 can be prepared by the reaction of N-nitroimines of Formula XVI with an alkylating agent of Formula XVII (Scheme 13) using procedures that are analogous to those described for Scheme 12.

30 Compounds of Formula XV can be prepared by the reaction of an alkylating agent of Formula XVIII with S-methyl-N-nitroisothiourea (Scheme 14) using procedures that are analogous to those described for Scheme 12.

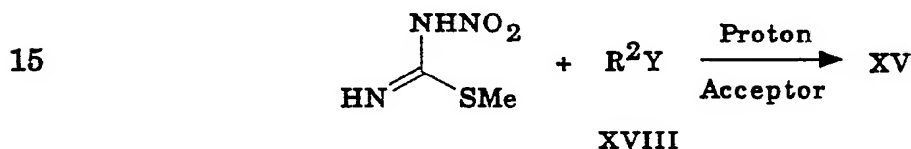
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Compounds of Formula XVI can be prepared by the reaction of an alkylating agent of Formula X with S-methyl-N-nitrosothiourea (Scheme 15) using procedures that are analogous to those described for Scheme 12.

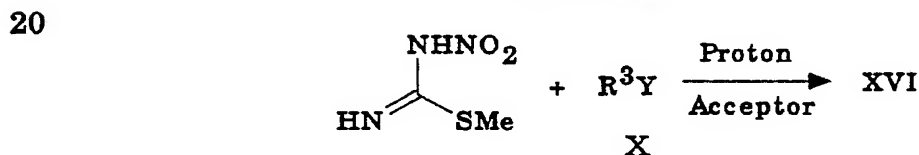
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SCHEME 13

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SCHEME 14

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SCHEME 15

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25 wherein:

R², R³, R⁴ and Y are as previously defined.

Compounds of Formula I where X is SO can be obtained by reaction of the corresponding compound of Formula I where X is S with a variety of oxidants including, but not limited to, peracids, periodates and hydroperoxides in a suitable solvent. Compounds of Formula I where X is SO₂ can be obtained using analogous reaction conditions wherein the amount of oxidant used is greater than or equal to two oxidizing equivalents.

30

The following Examples further illustrate the invention.

35

EXAMPLE 1**Step A: N-Methyl-2-(methylthio)ethanamine**

Solid 85% potassium hydroxide (54 g, 0.81 moles) was added in portions to a solution of methylamine hydrochloride (50 g, 0.74 moles) and water (200 mL), maintaining the temperature below 30°C. The resulting solution was treated with a solution of 2-chloroethyl methyl sulfide (15 mL, 0.15 moles) and ethanol (50 mL) at room temperature. After 1 hour, the temperature of the initially two-phase reaction had risen to about 40°C and the reaction became homogeneous. After stirring for 10 hours at room temperature, the reaction was saturated with solid sodium chloride and the aqueous layer was extracted with ether (3 x 100 mL). The combined organic layers were washed with brine made basic with potassium hydroxide, dried over potassium carbonate and concentrated under vacuum to yield 11.1 g (70%) of a clear oil that was used without further purification.

¹H NMR (200 MHz, CDCl₃) δ: 2.80 (t, 2H), 2.65 (t, 2H), 2.46 (s, 3H), 2.11 (s, 3H), 1.5 (br s, 1H).

20 Step B: Methyl N-methyl-N-[2-(methylthio)ethyl]-2-nitro-ethanimidothioate

A solution of the amine from Step A (1.0 g, 9.5 mmoles), 1,1-bis(methylthio)-2-nitroethylene (1.9 g, 11.4 mmoles) and ethanol (34 mL) was heated at reflux for 5 hours and then cooled to room temperature.

25 The resulting mixture was dissolved in acetone, silica gel (5 g) was added and the solvent was removed under vacuum. The residue was chromatographed on silica gel eluting with 1:1 hexanes-ethyl acetate to give 0.76 g (30%) of a yellow oil.

30 ¹H NMR (200 MHz, CDCl₃) δ: 6.72 (s, 1H), 3.78 (t, 2H), 3.15 (s, 3H), 2.75 (t, 2H), 2.49 (s, 3H), 2.16 (s, 3H).

Step C: N,N'-Dimethyl-N-[2-(methylthio)ethyl]-2-nitro-1,1-ethenediamine

35 Aqueous sodium hydroxide (50%, 0.5 mL, 9.0 mmoles) was added to a solution of the product of Step B (0.4 g, 1.8 mmoles), methylamine

hydrochloride (0.6 g, 9 mmoles), ethanol (5 mL), tetrahydrofuran (2 mL) and water (1 mL). The resulting solution was stirred for 20 hours at room temperature and then silica gel (2 g) was added and the solvent was removed. Flash chromatography of the residue on silica gel using 5% ethanol in methylene chloride gave 0.36 g (98%) of the title compound as a yellow oil.

^1H NMR (200 MHz, CDCl_3) δ : 9.8 (br s, 1H), 6.56 (s, 1H), 3.42 (t, 2H), 3.05 (d, 3H), 2.94 (s, 3H), 2.73 (t, 2H), 2.13 (s, 3H).

EXAMPLE 2

Step A: 2-(Nitromethylene)-imidazolidine

A solution of 4.0 mL (0.06 moles) of ethylene diamine, 10 g (0.06 moles) of 2,2 bis(methylthio)nitroethylene and 60 mL of ethanol was heated at reflux for 12h and then concentrated to give 7.6 g of a beige solid.

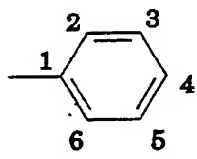
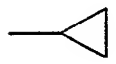
^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ : 6.33 (s, 1H), 3.58 (s, 4H).

Step B: 1-[2-(Methylthio)ethyl]-2-(nitroethylene)imidazolidine

The product from Step A (2.0 g, 0.016 moles) was added to a suspension of 60% sodium hydride (0.7 g, 0.017 moles) and 31 mL of DMF at room temperature. The resulting mixture was stirred for 10 min and then 1.5 mL (0.016 moles) of 2-chloroethyl methyl sulfide was added. Resulting mixture was heated at 100°C for 12 h and then cooled to room temperature. Ethanol, 20 ml, was added and the reaction was concentrated at 70°C. The residue was dissolved in 50 mL of EtOH; 5 g of silica gel was added, and the mixture was concentrated. The residue was chromatographed on 100 g silica gel eluting with CH_2Cl_2 -EtOH-48% NH_4OH (20:1:0.1) to give 1.0 g of a brown oil that solidified on standing. Trituration of the solid with MeOH gave a light yellow solid; mp = 102-104°C.

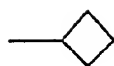
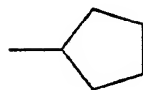
^1H NMR (400 MHz, CDCl_3) δ : 8.65 (br s, 1H), 6.55 (s, 1H), 3.78 (m, 4H), 3.38 (t, 2H), 2.70 (t, 2H), 2.16 (s, 3H).

In Tables 1 through 33, the following notations have been used:

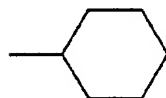
| | | | |
|----|-----------|---|--|
| 5 | allyl | = | $\text{CH}_2\text{CH}=\text{CH}_2$ |
| | propargyl | = | $\text{CH}_2\text{C}\equiv\text{CH}$ |
| | Me | = | $-\text{CH}_3$ |
| 10 | Et | = | $-\text{CH}_2-\text{CH}_3$ |
| | n-Pr | = | $-\text{CH}_2-\text{CH}_2-\text{CH}_3$ |
| 15 | i-Pr | = | $\begin{array}{c} -\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ |
| | n-Bu | = | $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ |
| 20 | i-Bu | = | $\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ |
| | s-Bu | = | $\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$ |
| 25 | t-Bu | = | $\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ |
| 30 | Ph | = |  |
| | c-Pr | = |  |

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5

c-Bu**=****c-pentyl****=**

10

c-hexyl**=**

15

20

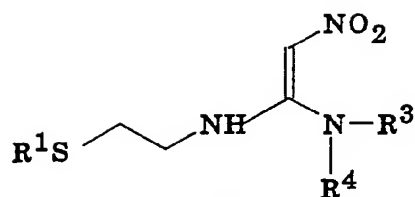
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TABLE 1

5



| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|--|----------------|
| 10 | Me | i-Pr | H | | Me | CH ₂ OC(CH ₃) ₂ OCH ₃ | H |
| | Me | n-Bu | H | | Me | SO ₂ CH ₃ | H |
| | Me | i-Bu | H | | Me | SO ₂ CH ₂ CH ₃ | H |
| | Me | s-Bu | H | | Me | SO ₂ CH ₂ CH ₂ CH ₃ | H |
| 15 | Me | t-Bu | H | | Me | CH ₂ CH ₂ SO ₂ CH ₃ | H |
| | Me | H | H | | Me | CH ₂ CHCH ₂ | H |
| | Me | COCH ₃ | H | | Me | CH ₂ CH ₂ CHCH ₂ | H |
| | Me | CHO | H | | Me | CH ₂ CHCHCH ₃ | H |
| | Me | COCH ₂ CH ₃ | H | | Me | CH ₂ CCH | H |
| 20 | Me | CH ₂ OCH ₃ | H | | Me | CH ₂ CH ₂ CCH | H |
| | Me | CH ₂ OCH ₂ CH ₃ | H | | Me | CH ₂ CCCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ CH ₃ | H | | Me | CH ₂ CN | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | H | | Me | NHCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₃ | H | | Me | NHCH ₂ CH ₃ | H |
| 25 | Me | OCH ₃ | H | | Me | NHCH(CH ₃) ₂ | H |
| | Me | OCH ₂ CH ₃ | H | | Me | NHC(CH ₃) ₃ | H |
| | Me | OCH ₂ CH ₂ CH ₃ | H | | Me | NHCH ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | OCH(CH ₃) ₂ | H | | Me | NHCH ₂ CH ₂ CH ₃ | H |
| | Me | CH ₂ OCH(CH ₃)OCH ₃ | H | | Me | N(CH ₃) ₂ | H |
| 30 | | | | | Me | N(CH ₃)CH ₂ CH ₃ | H |
| | | | | | Me | N(CH ₂ CH ₃) ₂ | H |
| | | | | | Me | CH ₂ Ph | H |
| | | | | | Me | Et | Me |
| | | | | | Me | n-Pr | Me |
| 35 | | | | | Me | i-Pr | Me |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|----|---|----------------|----------------|
| 5 | Me | n-Bu | Me | Me | OCH ₂ CH ₃ | Et | |
| | Me | COCH ₃ | Me | Me | SO ₂ CH ₃ | Et | |
| | Me | CHO | Me | Me | CH ₂ CH ₂ SO ₂ Me | Et | |
| | Me | COCH ₂ CH ₃ | Me | Me | CH ₂ CHCH ₂ | Et | |
| | Me | CH ₂ OCH ₃ | Me | Me | CH ₂ CCH | Et | |
| 10 | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Me | Me | CH ₂ CN | Et | |
| | Me | OCH ₃ | Me | Me | N(CH ₃) ₂ | Et | |
| | Me | OCH ₂ CH ₃ | Me | Me | n-Pr | n-Pr | |
| | Me | SO ₂ CH ₃ | Me | Me | i-Pr | i-Pr | |
| | Me | CH ₂ CH ₂ SO ₂ CH ₃ | Me | Me | COCH ₃ | n-Pr | |
| 15 | Me | CH ₂ CCH | Me | Me | CHO | n-Pr | |
| | Me | CH ₂ CN | Me | Me | COCH ₂ CH ₃ | n-Pr | |
| | Me | NHCH ₃ | Me | Me | CH ₂ OCH ₃ | n-Pr | |
| | Me | N(CH ₃) ₂ | Me | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Pr | |
| | Me | Et | Et | Me | OCH ₃ | n-Pr | |
| 20 | Me | COCH ₃ | Et | Me | OCH ₂ CH ₃ | n-Pr | |
| | Me | CHO | Et | Me | SO ₂ CH ₃ | n-Pr | |
| | Me | COCH ₂ CH ₃ | Et | Me | CH ₂ CH ₂ SO ₂ CH ₃ | n-Pr | |
| | Me | CH ₂ OCH ₃ | Et | Me | CH ₂ CN | n-Pr | |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Et | Me | N(CH ₃) ₂ | n-Pr | |
| 25 | Me | OCH ₃ | Et | | | | |

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| | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|
| 5 | Me | COCH ₃ | n-Bu |
| | Me | CHO | n-Bu |
| | Me | COCH ₂ CH ₃ | n-Bu |
| | Me | CH ₂ OCH ₃ | n-Bu |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Bu |
| 10 | Me | OCH ₃ | n-Bu |
| | Me | SO ₂ CH ₃ | n-Bu |
| | Me | CH ₂ CN | n-Bu |
| | Me | Me | c-Pr |
| | Me | Et | c-Pr |
| 15 | Me | n-Pr | c-Pr |
| | Me | OCH ₃ | c-Pr |
| | Me | CH ₂ CHCH ₂ | c-Pr |
| | Me | CH ₂ CCH | c-Pr |
| | Me | N(CH ₃) ₂ | c-Pr |
| 20 | Me | Me | c-Bu |
| | Me | Et | c-Bu |
| | Me | n-Pr | c-Bu |
| | Me | OCH ₃ | c-Bu |

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| R ¹ | R ³ | R ⁴ |
|----------------|-----------------------------------|------------------------------------|
| Me | CH ₂ CHCH ₂ | c-Bu |
| Me | CH ₂ CCH | c-Bu |
| Me | N(CH ₃) ₂ | c-Bu |
| Me | H | (CH ₂) ₃ Cl |
| Me | Me | (CH ₂) ₃ Cl |
| Me | Et | (CH ₂) ₃ Cl |
| Me | OCH ₃ | (CH ₂) ₃ Cl |
| Me | H | c-pentyl |
| Me | Me | c-pentyl |
| Me | Et | c-pentyl |
| Me | OCH ₃ | c-pentyl |
| Me | CH ₂ CHCH ₂ | c-pentyl |
| Me | CH ₂ CCH | c-pentyl |
| Me | CH ₂ Ph | c-pentyl |
| Me | H | c-hexyl |
| Me | Me | c-hexyl |
| Me | Et | c-hexyl |
| Me | OCH ₃ | c-hexyl |
| Me | CH ₂ CHCH ₂ | c-hexyl |
| Me | CH ₂ CCH | c-hexyl |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|----------------------------------|--------------------------------------|--|----------------|---|----------------|
| 5 | Me | CH ₂ Ph | CH ₂ -c-Pr | | Et | CH ₂ OCH ₃ | H |
| | Me | COCH ₃ | CH ₂ -c-Pr | | Et | (CH ₂) ₂ OCH ₂ CH ₃ | H |
| | Me | CHO | CH ₂ -c-Pr | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | H |
| | Me | CH ₂ OCH ₃ | CH ₂ -c-Pr | | Et | OCH ₃ | H |
| | Me | SO ₂ CH ₃ | CH ₂ -c-Pr | | Et | OCH ₂ CH ₃ | H |
| 10 | Me | CH ₂ CN | CH ₂ -c-Pr | | Et | SO ₂ CH ₃ | H |
| | Me | H | CH ₂ C(Cl)CH ₂ | | Et | (CH ₂) ₂ SO ₂ CH ₃ | H |
| | Me | Me | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CHCH ₂ | H |
| | Me | Et | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CHCHCH ₃ | H |
| | Me | n-Pr | CH ₂ C(Cl)CH ₂ | | Et | (CH ₂) ₂ CHCH ₂ | H |
| 15 | Me | CHO | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CCH | H |
| | Me | OCH ₃ | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CCCH ₃ | H |
| | Me | SO ₂ CH ₃ | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CN | H |
| | Me | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ | | Et | NHCH ₃ | H |
| | Et | H | H | | Et | N(CH ₃) ₂ | H |
| 20 | Et | Me | H | | Et | CH ₂ Ph | H |
| | Et | Et | H | | Et | Et | Me |
| | Et | n-Pr | H | | Et | n-Pr | Me |
| | Et | i-Pr | H | | Et | Me | Me |
| | Et | n-Bu | H | | Et | COCH ₃ | Me |
| 25 | Et | i-Bu | H | | Et | CHO | Me |
| | Et | s-Bu | H | | Et | CH ₂ OCH ₃ | Me |
| | Et | t-Bu | H | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Me |
| | Et | COCH ₃ | H | | Et | OCH ₃ | Me |
| | Et | CHO | H | | Et | SO ₂ CH ₃ | Me |
| 30 | | | | | | | |
| 35 | | | | | | | |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Et | (CH ₂) ₂ SO ₂ CH ₃ | Me | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Pr |
| | Et | CH ₂ CHCH ₂ | Me | | Et | OCH ₃ | n-Pr |
| | Et | CH ₂ CCH | Me | | Et | SO ₂ CH ₃ | n-Pr |
| | Et | CH ₂ CN | Me | | Et | (CH ₂) ₂ SO ₂ CH ₃ | n-Pr |
| | Et | NHCH ₃ | Me | | Et | CH ₂ CHCH ₂ | n-Pr |
| 10 | Et | N(CH ₃) ₂ | Me | | Et | CH ₂ CCH | n-Pr |
| | Et | CH ₂ Ph | Me | | Et | CH ₂ CN | n-Pr |
| | Et | Et | Et | | Et | N(CH ₃) ₂ | n-Pr |
| | Et | COCH ₃ | Et | | Et | CH ₂ Ph | n-Pr |
| | Et | CHO | Et | | Et | n-Bu | n-Bu |
| 15 | Et | CH ₂ OCH ₃ | Et | | Et | CHO | n-Bu |
| | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Et | | Et | COCH ₃ | n-Bu |
| | Et | OCH ₃ | Et | | Et | CH ₂ OCH ₃ | n-Bu |
| | Et | SO ₂ CH ₃ | Et | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Bu |
| | Et | (CH ₂) ₂ SO ₂ CH ₃ | Et | | Et | OCH ₃ | n-Bu |
| 20 | Et | CH ₂ CCH | Et | | Et | SO ₂ CH ₃ | n-Bu |
| | Et | CH ₂ CHCH ₂ | Et | | Et | CH ₂ CN | n-Bu |
| | Et | CH ₂ CN | Et | | Et | CH ₂ Ph | n-Bu |
| | Et | N(CH ₃) ₂ | Et | | Et | i-Pr | i-Pr |
| | Et | CH ₂ Ph | Et | | Et | Me | c-Pr |
| 25 | Et | n-Pr | n-Pr | | Et | Et | c-Pr |
| | Et | CHO | n-Pr | | Et | n-Pr | c-Pr |
| | Et | COCH ₃ | n-Pr | | Et | OCH ₃ | c-Pr |
| | Et | CH ₂ OCH ₃ | n-Pr | | Et | CH ₂ CHCH ₂ | c-Pr |

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|-----------------------------------|------------------------------------|--|----------------|----------------------------------|--------------------------------------|
| 5 | Et | CH ₂ CCH | c-Pr | | Et | CH ₂ CCH | c-hexyl |
| | Et | N(CH ₃) ₂ | c-Pr | | Et | CH ₂ Ph | c-hexyl |
| | Et | CH ₂ Ph | c-Pr | | Et | CH ₂ Ph | CH ₂ -c-Pr |
| | Et | H | c-Pr | | Et | CHO | CH ₂ -c-Pr |
| | Et | H | c-Bu | | Et | CH ₂ OCH ₃ | CH ₂ -c-Pr |
| 10 | Et | Me | c-Bu | | Et | SO ₂ CH ₃ | CH ₂ -c-Pr |
| | Et | OCH ₃ | c-Bu | | Et | CH ₂ CN | CH ₂ -c-Pr |
| | Et | N(CH ₃) ₂ | c-Bu | | Et | H | CH ₂ C(Cl)CH ₂ |
| | Et | CH ₂ Ph | c-Bu | | Et | Me | CH ₂ C(Cl)CH ₂ |
| | Et | H | (CH ₂) ₃ Cl | | Et | Et | CH ₂ C(Cl)CH ₂ |
| 15 | Et | Me | (CH ₂) ₃ Cl | | Et | n-Pr | CH ₂ C(Cl)CH ₂ |
| | Et | OCH ₃ | (CH ₂) ₃ Cl | | Et | OCH ₃ | CH ₂ C(Cl)CH ₂ |
| | Et | CH ₂ Ph | (CH ₂) ₃ Cl | | Et | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ |
| | Et | H | c-pentyl | | n-Pr | H | H |
| | Et | Me | c-pentyl | | n-Pr | Me | H |
| 20 | Et | Et | c-pentyl | | n-Pr | Et | H |
| | Et | OCH ₃ | c-pentyl | | n-Pr | n-Pr | H |
| | Et | CH ₂ CHCH ₂ | c-pentyl | | n-Pr | i-Pr | H |
| | Et | CH ₂ CCH | c-pentyl | | n-Pr | n-Bu | H |
| | Et | CH ₂ Ph | c-pentyl | | n-Pr | i-Bu | H |
| 25 | Et | H | c-hexyl | | n-Pr | s-Bu | H |
| | Et | Me | c-hexyl | | n-Pr | t-Bu | H |
| | Et | Et | c-hexyl | | n-Pr | CHO | H |
| | Et | OCH ₃ | c-hexyl | | n-Pr | COCH ₃ | H |
| | Et | CH ₂ CHCH ₂ | c-hexyl | | n-Pr | CH ₂ OCH ₃ | H |

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| | R ¹ | R ³ | R ⁴ | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|------------------------------------|---------------------------------|--------------------------------------|
| 5 | n-Pr | OCH ₃ | H | n-Pr | CH ₂ Ph | n-Pr |
| | n-Pr | SO ₂ CH ₃ | H | n-Pr | n-Bu | n-Bu |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | H | n-Pr | CHO | n-Bu |
| | n-Pr | CH ₂ CHCH ₂ | H | n-Pr | SO ₂ CH ₃ | n-Bu |
| | n-Pr | CH ₂ CCH | H | n-Pr | CH ₂ CN | n-Bu |
| 10 | n-Pr | CH ₂ CN | H | n-Pr | CH ₂ Ph | n-Bu |
| | n-Pr | N(CH ₃) ₂ | H | n-Pr | Me | c-Pr |
| | n-Pr | CH ₂ Ph | H | n-Pr | H | c-Pr |
| | n-Pr | Me | Me | n-Pr | H | (CH ₂) ₃ Cl |
| | n-Pr | CHO | Me | n-Pr | H | c-pentyl |
| 15 | n-Pr | COCH ₃ | Me | n-Pr | H | c-hexyl |
| | n-Pr | OCH ₃ | Me | n-Pr | H | CH ₂ C(Cl)CH ₂ |
| | n-Pr | SO ₂ CH ₃ | Me | n-Pr | H | CH ₂ -c-Pr |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | Me | n-Bu | Me | H |
| | n-Pr | CH ₂ CN | Me | CH ₂ CH ₂ Cl | Me | H |
| 20 | n-Pr | CH ₂ Ph | Me | (CH ₂) ₃ Cl | Me | H |
| | n-Pr | Et | Et | (CH ₂) ₄ Cl | Me | H |
| | n-Pr | CHO | Et | c-Pr | Me | H |
| | n-Pr | COCH ₃ | Et | c-Bu | Me | H |
| | n-Pr | OCH ₃ | Et | i-Pr | Me | H |
| 25 | n-Pr | SO ₂ CH ₃ | Et | c-pentyl | Me | H |
| | n-Pr | CH ₂ CN | Et | c-hexyl | Me | H |
| | n-Pr | CH ₂ Ph | Et | CH ₂ -c-Pr | Me | H |
| | n-Pr | i-Pr | i-Pr | CH ₂ -c-pentyl | Me | H |
| | n-Pr | CHO | n- | | | |
| 30 | Pr | | | | | |
| | n-Pr | SO ₂ CH ₃ | n- | | | |
| | Pr | | | | | |

TABLE 2

5

$$\begin{array}{c}
 \text{NO}_2 \\
 | \\
 \text{N} \\
 || \\
 \text{R}^1\text{S}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}-\text{N}-\text{R}^3 \\
 | \\
 \text{R}^4
 \end{array}$$

| | | | | | | |
|----|----------------|---|----------------|----------------|--|----------------|
| 10 | R ¹ | R ³ | R ⁴ | R ¹ | R ³ | R ⁴ |
| | Me | i-Pr | H | Me | CH ₂ OC(CH ₃) ₂ OCH ₃ | H |
| | Me | n-Bu | H | Me | SO ₂ CH ₃ | H |
| | Me | i-Bu | H | Me | SO ₂ CH ₂ CH ₃ | H |
| | Me | s-Bu | H | Me | SO ₂ CH ₂ CH ₂ CH ₃ | H |
| 15 | Me | t-Bu | H | Me | CH ₂ CH ₂ SO ₂ CH ₃ | H |
| | Me | H | H | Me | CH ₂ CHCH ₂ | H |
| | Me | COCH ₃ | H | Me | CH ₂ CH ₂ CHCH ₂ | H |
| | Me | CHO | H | Me | CH ₂ CHCHCH ₃ | H |
| | Me | COCH ₂ CH ₃ | H | Me | CH ₂ CCH | H |
| 20 | Me | CH ₂ OCH ₃ | H | Me | CH ₂ CH ₂ CCH | H |
| | Me | CH ₂ OCH ₂ CH ₃ | H | Me | CH ₂ CCCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ CH ₃ | H | Me | CH ₂ CN | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | H | Me | NHCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₃ | H | Me | NHCH ₂ CH ₃ | H |
| 25 | Me | OCH ₃ | H | Me | NHCH(CH ₃) ₂ | H |
| | Me | OCH ₂ CH ₃ | H | Me | NHC(CH ₃) ₃ | H |
| | Me | OCH ₂ CH ₂ CH ₃ | H | Me | NHCH ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | OCH(CH ₃) ₂ | H | Me | NHCH ₂ CH ₂ CH ₃ | H |
| | Me | CH ₂ OCH(CH ₃)OCH ₃ | H | Me | N(CH ₃) ₂ | H |
| 30 | | | | Me | N(CH ₃)CH ₂ CH ₃ | H |
| | | | | Me | N(CH ₂ CH ₃) ₂ | H |
| | | | | Me | CH ₂ Ph | H |
| | | | | Me | Et | Me |
| | | | | Me | n-Pr | Me |
| 35 | | | | Me | i-Pr | Me |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|----|---|----------------|----------------|
| 5 | Me | n-Bu | Me | Me | OCH ₂ CH ₃ | Et | |
| | Me | COCH ₃ | Me | Me | SO ₂ CH ₃ | Et | |
| | Me | CHO | Me | Me | CH ₂ CH ₂ SO ₂ Me | Et | |
| | Me | COCH ₂ CH ₃ | Me | Me | CH ₂ CHCH ₂ | Et | |
| | Me | CH ₂ OCH ₃ | Me | Me | CH ₂ CCH | Et | |
| 10 | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Me | Me | CH ₂ CN | Et | |
| | Me | OCH ₃ | Me | Me | N(CH ₃) ₂ | Et | |
| | Me | OCH ₂ CH ₃ | Me | Me | n-Pr | n-Pr | |
| | Me | SO ₂ CH ₃ | Me | Me | i-Pr | i-Pr | |
| | Me | CH ₂ CH ₂ SO ₂ CH ₃ | Me | Me | COCH ₃ | n-Pr | |
| 15 | Me | CH ₂ CCH | Me | Me | CHO | n-Pr | |
| | Me | CH ₂ CN | Me | Me | COCH ₂ CH ₃ | n-Pr | |
| | Me | NHCH ₃ | Me | Me | CH ₂ OCH ₃ | n-Pr | |
| | Me | N(CH ₃) ₂ | Me | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Pr | |
| | Me | Et | Et | Me | OCH ₃ | n-Pr | |
| 20 | Me | COCH ₃ | Et | Me | OCH ₂ CH ₃ | n-Pr | |
| | Me | CHO | Et | Me | SO ₂ CH ₃ | n-Pr | |
| | Me | COCH ₂ CH ₃ | Et | Me | CH ₂ CH ₂ SO ₂ CH ₃ | n-Pr | |
| | Me | CH ₂ OCH ₃ | Et | Me | CH ₂ CN | n-Pr | |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Et | Me | N(CH ₃) ₂ | n-Pr | |
| 25 | Me | OCH ₃ | Et | | | | |

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| | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|
| 5 | Me | COCH ₃ | n-Bu |
| | Me | CHO | n-Bu |
| | Me | COCH ₂ CH ₃ | n-Bu |
| | Me | CH ₂ OCH ₃ | n-Bu |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Bu |
| 10 | Me | OCH ₃ | n-Bu |
| | Me | SO ₂ CH ₃ | n-Bu |
| | Me | CH ₂ CN | n-Bu |
| | Me | Me | c-Pr |
| | Me | Et | c-Pr |
| 15 | Me | n-Pr | c-Pr |
| | Me | OCH ₃ | c-Pr |
| | Me | CH ₂ CHCH ₂ | c-Pr |
| | Me | CH ₂ CCH | c-Pr |
| | Me | N(CH ₃) ₂ | c-Pr |
| 20 | Me | Me | c-Bu |
| | Me | Et | c-Bu |
| | Me | n-Pr | c-Bu |
| | Me | OCH ₃ | c-Bu |

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| R ¹ | R ³ | R ⁴ |
|----------------|-----------------------------------|------------------------------------|
| Me | CH ₂ CHCH ₂ | c-Bu |
| Me | CH ₂ CCH | c-Bu |
| Me | N(CH ₃) ₂ | c-Bu |
| Me | H | (CH ₂) ₃ Cl |
| Me | Me | (CH ₂) ₃ Cl |
| Me | Et | (CH ₂) ₃ Cl |
| Me | OCH ₃ | (CH ₂) ₃ Cl |
| Me | H | c-pentyl |
| Me | Me | c-pentyl |
| Me | Et | c-pentyl |
| Me | OCH ₃ | c-pentyl |
| Me | CH ₂ CHCH ₂ | c-pentyl |
| Me | CH ₂ CCH | c-pentyl |
| Me | CH ₂ Ph | c-pentyl |
| Me | H | c-hexyl |
| Me | Me | c-hexyl |
| Me | Et | c-hexyl |
| Me | OCH ₃ | c-hexyl |
| Me | CH ₂ CHCH ₂ | c-hexyl |
| Me | CH ₂ CCH | c-hexyl |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|----------------------------------|--------------------------------------|--|----------------|---|----------------|
| 5 | Me | CH ₂ Ph | CH ₂ -c-Pr | | Et | CH ₂ OCH ₃ | H |
| | Me | COCH ₃ | CH ₂ -c-Pr | | Et | (CH ₂) ₂ OCH ₂ CH ₃ | H |
| | Me | CHO | CH ₂ -c-Pr | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | H |
| | Me | CH ₂ OCH ₃ | CH ₂ -c-Pr | | Et | OCH ₃ | H |
| | Me | SO ₂ CH ₃ | CH ₂ -c-Pr | | Et | OCH ₂ CH ₃ | H |
| 10 | Me | CH ₂ CN | CH ₂ -c-Pr | | Et | SO ₂ CH ₃ | H |
| | Me | H | CH ₂ C(Cl)CH ₂ | | Et | (CH ₂) ₂ SO ₂ CH ₃ | H |
| | Me | Me | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CHCH ₂ | H |
| | Me | Et | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CHCHCH ₃ | H |
| | Me | n-Pr | CH ₂ C(Cl)CH ₂ | | Et | (CH ₂) ₂ CHCH ₂ | H |
| 15 | Me | CHO | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CCH | H |
| | Me | OCH ₃ | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CCCH ₃ | H |
| | Me | SO ₂ CH ₃ | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CN | H |
| | Me | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ | | Et | NHCH ₃ | H |
| | Et | H | H | | Et | N(CH ₃) ₂ | H |
| 20 | Et | Me | H | | Et | CH ₂ Ph | H |
| | Et | Et | H | | Et | Et | Me |
| | Et | n-Pr | H | | Et | n-Pr | Me |
| | Et | i-Pr | H | | Et | Me | Me |
| | Et | n-Bu | H | | Et | COCH ₃ | Me |
| 25 | Et | i-Bu | H | | Et | CHO | Me |
| | Et | s-Bu | H | | Et | CH ₂ OCH ₃ | Me |
| | Et | t-Bu | H | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Me |
| | Et | COCH ₃ | H | | Et | OCH ₃ | Me |
| | Et | CHO | H | | Et | SO ₂ CH ₃ | Me |

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Et | (CH ₂) ₂ SO ₂ CH ₃ | Me | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Pr |
| | Et | CH ₂ CHCH ₂ | Me | | Et | OCH ₃ | n-Pr |
| | Et | CH ₂ CCH | Me | | Et | SO ₂ CH ₃ | n-Pr |
| | Et | CH ₂ CN | Me | | Et | (CH ₂) ₂ SO ₂ CH ₃ | n-Pr |
| | Et | NHCH ₃ | Me | | Et | CH ₂ CHCH ₂ | n-Pr |
| 10 | Et | N(CH ₃) ₂ | Me | | Et | CH ₂ CCH | n-Pr |
| | Et | CH ₂ Ph | Me | | Et | CH ₂ CN | n-Pr |
| | Et | Et | Et | | Et | N(CH ₃) ₂ | n-Pr |
| | Et | COCH ₃ | Et | | Et | CH ₂ Ph | n-Pr |
| | Et | CHO | Et | | Et | n-Bu | n-Bu |
| 15 | Et | CH ₂ OCH ₃ | Et | | Et | CHO | n-Bu |
| | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Et | | Et | COCH ₃ | n-Bu |
| | Et | OCH ₃ | Et | | Et | CH ₂ OCH ₃ | n-Bu |
| | Et | SO ₂ CH ₃ | Et | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Bu |
| | Et | (CH ₂) ₂ SO ₂ CH ₃ | Et | | Et | OCH ₃ | n-Bu |
| 20 | Et | CH ₂ CCH | Et | | Et | SO ₂ CH ₃ | n-Bu |
| | Et | CH ₂ CHCH ₂ | Et | | Et | CH ₂ CN | n-Bu |
| | Et | CH ₂ CN | Et | | Et | CH ₂ Ph | n-Bu |
| | Et | N(CH ₃) ₂ | Et | | Et | i-Pr | i-Pr |
| | Et | CH ₂ Ph | Et | | Et | Me | c-Pr |
| 25 | Et | n-Pr | n-Pr | | Et | Et | c-Pr |
| | Et | CHO | n-Pr | | Et | n-Pr | c-Pr |
| | Et | COCH ₃ | n-Pr | | Et | OCH ₃ | c-Pr |
| | Et | CH ₂ OCH ₃ | n-Pr | | Et | CH ₂ CHCH ₂ | c-Pr |

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| | R ¹ | R ³ | R ⁴ |
|----|----------------|-----------------------------------|------------------------------------|
| 5 | Et | CH ₂ CCH | c-Pr |
| | Et | N(CH ₃) ₂ | c-Pr |
| | Et | CH ₂ Ph | c-Pr |
| | Et | H | c-Pr |
| | Et | H | c-Bu |
| 10 | Et | Me | c-Bu |
| | Et | OCH ₃ | c-Bu |
| | Et | N(CH ₃) ₂ | c-Bu |
| | Et | CH ₂ Ph | c-Bu |
| | Et | H | (CH ₂) ₃ Cl |
| 15 | Et | Me | (CH ₂) ₃ Cl |
| | Et | OCH ₃ | (CH ₂) ₃ Cl |
| | Et | CH ₂ Ph | (CH ₂) ₃ Cl |
| | Et | H | c-pentyl |
| | Et | Me | c-pentyl |
| 20 | Et | Et | c-pentyl |
| | Et | OCH ₃ | c-pentyl |
| | Et | CH ₂ CHCH ₂ | c-pentyl |
| | Et | CH ₂ CCH | c-pentyl |
| | Et | CH ₂ Ph | c-pentyl |
| 25 | Et | H | c-hexyl |
| | Et | Me | c-hexyl |
| | Et | Et | c-hexyl |
| | Et | OCH ₃ | c-hexyl |
| | Et | CH ₂ CHCH ₂ | c-hexyl |

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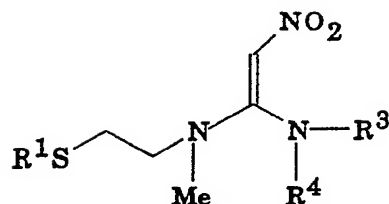
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| R ¹ | R ³ | R ⁴ |
|----------------|----------------------------------|--------------------------------------|
| Et | CH ₂ CCH | c-hexyl |
| Et | CH ₂ Ph | c-hexyl |
| Et | CH ₂ Ph | CH ₂ -c-Pr |
| Et | CHO | CH ₂ -c-Pr |
| Et | CH ₂ OCH ₃ | CH ₂ -c-Pr |
| Et | SO ₂ CH ₃ | CH ₂ -c-Pr |
| Et | CH ₂ CN | CH ₂ -c-Pr |
| Et | H | CH ₂ C(Cl)CH ₂ |
| Et | Me | CH ₂ C(Cl)CH ₂ |
| Et | Et | CH ₂ C(Cl)CH ₂ |
| Et | n-Pr | CH ₂ C(Cl)CH ₂ |
| Et | OCH ₃ | CH ₂ C(Cl)CH ₂ |
| Et | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ |
| n-Pr | H | H |
| n-Pr | Me | H |
| n-Pr | Et | H |
| n-Pr | n-Pr | H |
| n-Pr | i-Pr | H |
| n-Pr | n-Bu | H |
| n-Pr | i-Bu | H |
| n-Pr | s-Bu | H |
| n-Pr | t-Bu | H |
| n-Pr | CHO | H |
| n-Pr | COCH ₃ | H |
| n-Pr | CH ₂ OCH ₃ | H |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|------------------------------------|---------------------------------|--------------------------------------|----------------|
| 5 | n-Pr | OCH ₃ | H | n-Pr | CH ₂ Ph | n-Pr | |
| | n-Pr | SO ₂ CH ₃ | H | n-Pr | n-Bu | n-Bu | |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | H | n-Pr | CHO | n-Bu | |
| | n-Pr | CH ₂ CHCH ₂ | H | n-Pr | SO ₂ CH ₃ | n-Bu | |
| | n-Pr | CH ₂ CCH | H | n-Pr | CH ₂ CN | n-Bu | |
| 10 | n-Pr | CH ₂ CN | H | n-Pr | CH ₂ Ph | n-Bu | |
| | n-Pr | N(CH ₃) ₂ | H | n-Pr | Me | c-Pr | |
| | n-Pr | CH ₂ Ph | H | n-Pr | H | c-Pr | |
| | n-Pr | Me | Me | n-Pr | H | (CH ₂) ₃ Cl | |
| 15 | n-Pr | CHO | Me | n-Pr | H | c-pentyl | |
| | n-Pr | COCH ₃ | Me | n-Pr | H | c-hexyl | |
| | n-Pr | OCH ₃ | Me | n-Pr | H | CH ₂ C(Cl)CH ₂ | |
| | n-Pr | SO ₂ CH ₃ | Me | n-Pr | H | CH ₂ -c-Pr | |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | Me | n-Bu | Me | H | |
| | n-Pr | CH ₂ CN | Me | CH ₂ CH ₂ Cl | Me | H | |
| | n-Pr | CH ₂ Ph | Me | (CH ₂) ₃ Cl | Me | H | |
| | n-Pr | Et | Et | (CH ₂) ₄ Cl | Me | H | |
| 20 | n-Pr | CHO | Et | c-Pr | Me | H | |
| | n-Pr | COCH ₃ | Et | c-Bu | Me | H | |
| | n-Pr | OCH ₃ | Et | i-Pr | Me | H | |
| | n-Pr | SO ₂ CH ₃ | Et | c-pentyl | Me | H | |
| | n-Pr | CH ₂ CN | Et | c-hexyl | Me | H | |
| | n-Pr | CH ₂ Ph | Et | CH ₂ -c-Pr | Me | H | |
| 25 | n-Pr | i-Pr | i-Pr | CH ₂ -c-pentyl | Me | H | |
| | n-Pr | CHO | n- | | | | |
| 30 | Pr | | | | | | |
| | n-Pr | SO ₂ CH ₃ | n- | | | | |
| | Pr | | | | | | |

TABLE 3

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|--|----------------|
| 10 | Me | i-Pr | H | | Me | CH ₂ OC(CH ₃) ₂ OCH ₃ | H |
| | Me | n-Bu | H | | Me | SO ₂ CH ₃ | H |
| | Me | i-Bu | H | | Me | SO ₂ CH ₂ CH ₃ | H |
| | Me | s-Bu | H | | Me | SO ₂ CH ₂ CH ₂ CH ₃ | H |
| 15 | Me | t-Bu | H | | Me | CH ₂ CH ₂ SO ₂ CH ₃ | H |
| | Me | H | H | | Me | CH ₂ CHCH ₂ | H |
| | Me | COCH ₃ | H | | Me | CH ₂ CH ₂ CHCH ₂ | H |
| | Me | CHO | H | | Me | CH ₂ CHCHCH ₃ | H |
| | Me | COCH ₂ CH ₃ | H | | Me | CH ₂ CCH | H |
| 20 | Me | CH ₂ OCH ₃ | H | | Me | CH ₂ CH ₂ CCH | H |
| | Me | CH ₂ OCH ₂ CH ₃ | H | | Me | CH ₂ CCCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ CH ₃ | H | | Me | CH ₂ CN | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | H | | Me | NHCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₃ | H | | Me | NHCH ₂ CH ₃ | H |
| 25 | Me | OCH ₃ | H | | Me | NHCH(CH ₃) ₂ | H |
| | Me | OCH ₂ CH ₃ | H | | Me | NHC(CH ₃) ₃ | H |
| | Me | OCH ₂ CH ₂ CH ₃ | H | | Me | NHCH ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | OCH(CH ₃) ₂ | H | | Me | NHCH ₂ CH ₂ CH ₃ | H |
| 30 | Me | CH ₂ OCH(CH ₃)OCH ₃ | H | | Me | N(CH ₃) ₂ | H |
| | | | | | Me | N(CH ₃)CH ₂ CH ₃ | H |
| | | | | | Me | N(CH ₂ CH ₃) ₂ | H |
| | | | | | Me | CH ₂ Ph | H |
| | | | | | Me | Et | Me |
| 35 | | | | | Me | n-Pr | Me |
| | | | | | Me | i-Pr | Me |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|----|---|----------------|----------------|
| 5 | Me | n-Bu | Me | Me | OCH ₂ CH ₃ | Et | |
| | Me | COCH ₃ | Me | Me | SO ₂ CH ₃ | Et | |
| | Me | CHO | Me | Me | CH ₂ CH ₂ SO ₂ Me | Et | |
| | Me | COCH ₂ CH ₃ | Me | Me | CH ₂ CHCH ₂ | Et | |
| | Me | CH ₂ OCH ₃ | Me | Me | CH ₂ CCH | Et | |
| 10 | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Me | Me | CH ₂ CN | Et | |
| | Me | OCH ₃ | Me | Me | N(CH ₃) ₂ | Et | |
| | Me | OCH ₂ CH ₃ | Me | Me | n-Pr | n-Pr | |
| | Me | SO ₂ CH ₃ | Me | Me | i-Pr | i-Pr | |
| | Me | CH ₂ CH ₂ SO ₂ CH ₃ | Me | Me | COCH ₃ | n-Pr | |
| 15 | Me | CH ₂ CCH | Me | Me | CHO | n-Pr | |
| | Me | CH ₂ CN | Me | Me | COCH ₂ CH ₃ | n-Pr | |
| | Me | NHCH ₃ | Me | Me | CH ₂ OCH ₃ | n-Pr | |
| | Me | N(CH ₃) ₂ | Me | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Pr | |
| | Me | Et | Et | Me | OCH ₃ | n-Pr | |
| 20 | Me | COCH ₃ | Et | Me | OCH ₂ CH ₃ | n-Pr | |
| | Me | CHO | Et | Me | SO ₂ CH ₃ | n-Pr | |
| | Me | COCH ₂ CH ₃ | Et | Me | CH ₂ CH ₂ SO ₂ CH ₃ | n-Pr | |
| | Me | CH ₂ OCH ₃ | Et | Me | CH ₂ CN | n-Pr | |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Et | Me | N(CH ₃) ₂ | n-Pr | |
| 25 | Me | OCH ₃ | Et | | | | |

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| | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|
| 5 | Me | COCH ₃ | n-Bu |
| | Me | CHO | n-Bu |
| | Me | COCH ₂ CH ₃ | n-Bu |
| | Me | CH ₂ OCH ₃ | n-Bu |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Bu |
| 10 | Me | OCH ₃ | n-Bu |
| | Me | SO ₂ CH ₃ | n-Bu |
| | Me | CH ₂ CN | n-Bu |
| | Me | Me | c-Pr |
| | Me | Et | c-Pr |
| 15 | Me | n-Pr | c-Pr |
| | Me | OCH ₃ | c-Pr |
| | Me | CH ₂ CHCH ₂ | c-Pr |
| | Me | CH ₂ CCH | c-Pr |
| | Me | N(CH ₃) ₂ | c-Pr |
| 20 | Me | Me | c-Bu |
| | Me | Et | c-Bu |
| | Me | n-Pr | c-Bu |
| | Me | OCH ₃ | c-Bu |

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| R ¹ | R ³ | R ⁴ |
|----------------|-----------------------------------|------------------------------------|
| Me | CH ₂ CHCH ₂ | c-Bu |
| Me | CH ₂ CCH | c-Bu |
| Me | N(CH ₃) ₂ | c-Bu |
| Me | H | (CH ₂) ₃ Cl |
| Me | Me | (CH ₂) ₃ Cl |
| Me | Et | (CH ₂) ₃ Cl |
| Me | OCH ₃ | (CH ₂) ₃ Cl |
| Me | H | c-pentyl |
| Me | Me | c-pentyl |
| Me | Et | c-pentyl |
| Me | OCH ₃ | c-pentyl |
| Me | CH ₂ CHCH ₂ | c-pentyl |
| Me | CH ₂ CCH | c-pentyl |
| Me | CH ₂ Ph | c-pentyl |
| Me | H | c-hexyl |
| Me | Me | c-hexyl |
| Me | Et | c-hexyl |
| Me | OCH ₃ | c-hexyl |
| Me | CH ₂ CHCH ₂ | c-hexyl |
| Me | CH ₂ CCH | c-hexyl |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|----------------------------------|--------------------------------------|--|----------------|---|----------------|
| 5 | Me | CH ₂ Ph | CH ₂ -c-Pr | | Et | CH ₂ OCH ₃ | H |
| | Me | COCH ₃ | CH ₂ -c-Pr | | Et | (CH ₂) ₂ OCH ₂ CH ₃ | H |
| | Me | CHO | CH ₂ -c-Pr | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | H |
| | Me | CH ₂ OCH ₃ | CH ₂ -c-Pr | | Et | OCH ₃ | H |
| | Me | SO ₂ CH ₃ | CH ₂ -c-Pr | | Et | OCH ₂ CH ₃ | H |
| 10 | Me | CH ₂ CN | CH ₂ -c-Pr | | Et | SO ₂ CH ₃ | H |
| | Me | H | CH ₂ C(Cl)CH ₂ | | Et | (CH ₂) ₂ SO ₂ CH ₃ | H |
| | Me | Me | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CHCH ₂ | H |
| | Me | Et | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CHCHCH ₃ | H |
| | Me | n-Pr | CH ₂ C(Cl)CH ₂ | | Et | (CH ₂) ₂ CHCH ₂ | H |
| 15 | Me | CHO | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CCH | H |
| | Me | OCH ₃ | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CCCH ₃ | H |
| | Me | SO ₂ CH ₃ | CH ₂ C(Cl)CH ₂ | | Et | CH ₂ CN | H |
| | Me | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ | | Et | NHCH ₃ | H |
| | Et | H | H | | Et | N(CH ₃) ₂ | H |
| 20 | Et | Me | H | | Et | CH ₂ Ph | H |
| | Et | Et | H | | Et | Et | Me |
| | Et | n-Pr | H | | Et | n-Pr | Me |
| | Et | i-Pr | H | | Et | Me | Me |
| | Et | n-Bu | H | | Et | COCH ₃ | Me |
| 25 | Et | i-Bu | H | | Et | CHO | Me |
| | Et | s-Bu | H | | Et | CH ₂ OCH ₃ | Me |
| | Et | t-Bu | H | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Me |
| | Et | COCH ₃ | H | | Et | OCH ₃ | Me |
| | Et | CHO | H | | Et | SO ₂ CH ₃ | Me |

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Et | (CH ₂) ₂ SO ₂ CH ₃ | Me | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Pr |
| | Et | CH ₂ CHCH ₂ | Me | | Et | OCH ₃ | n-Pr |
| | Et | CH ₂ CCH | Me | | Et | SO ₂ CH ₃ | n-Pr |
| | Et | CH ₂ CN | Me | | Et | (CH ₂) ₂ SO ₂ CH ₃ | n-Pr |
| | Et | NHCH ₃ | Me | | Et | CH ₂ CHCH ₂ | n-Pr |
| 10 | Et | N(CH ₃) ₂ | Me | | Et | CH ₂ CCH | n-Pr |
| | Et | CH ₂ Ph | Me | | Et | CH ₂ CN | n-Pr |
| | Et | Et | Et | | Et | N(CH ₃) ₂ | n-Pr |
| | Et | COCH ₃ | Et | | Et | CH ₂ Ph | n-Pr |
| | Et | CHO | Et | | Et | n-Bu | n-Bu |
| 15 | Et | CH ₂ OCH ₃ | Et | | Et | CHO | n-Bu |
| | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Et | | Et | COCH ₃ | n-Bu |
| | Et | OCH ₃ | Et | | Et | CH ₂ OCH ₃ | n-Bu |
| | Et | SO ₂ CH ₃ | Et | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Bu |
| | Et | (CH ₂) ₂ SO ₂ CH ₃ | Et | | Et | OCH ₃ | n-Bu |
| 20 | Et | CH ₂ CCH | Et | | Et | SO ₂ CH ₃ | n-Bu |
| | Et | CH ₂ CHCH ₂ | Et | | Et | CH ₂ CN | n-Bu |
| | Et | CH ₂ CN | Et | | Et | CH ₂ Ph | n-Bu |
| | Et | N(CH ₃) ₂ | Et | | Et | i-Pr | i-Pr |
| | Et | CH ₂ Ph | Et | | Et | Me | c-Pr |
| 25 | Et | n-Pr | n-Pr | | Et | Et | c-Pr |
| | Et | CHO | n-Pr | | Et | n-Pr | c-Pr |
| | Et | COCH ₃ | n-Pr | | Et | OCH ₃ | c-Pr |
| | Et | CH ₂ OCH ₃ | n-Pr | | Et | CH ₂ CHCH ₂ | c-Pr |

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|-----------------------------------|------------------------------------|--|----------------|----------------------------------|--------------------------------------|
| 5 | Et | CH ₂ CCH | c-Pr | | Et | CH ₂ CCH | c-hexyl |
| | Et | N(CH ₃) ₂ | c-Pr | | Et | CH ₂ Ph | c-hexyl |
| | Et | CH ₂ Ph | c-Pr | | Et | CH ₂ Ph | CH ₂ -c-Pr |
| | Et | H | c-Pr | | Et | CHO | CH ₂ -c-Pr |
| | Et | H | c-Bu | | Et | CH ₂ OCH ₃ | CH ₂ -c-Pr |
| 10 | Et | Me | c-Bu | | Et | SO ₂ CH ₃ | CH ₂ -c-Pr |
| | Et | OCH ₃ | c-Bu | | Et | CH ₂ CN | CH ₂ -c-Pr |
| | Et | N(CH ₃) ₂ | c-Bu | | Et | H | CH ₂ C(Cl)CH ₂ |
| | Et | CH ₂ Ph | c-Bu | | Et | Me | CH ₂ C(Cl)CH ₂ |
| | Et | H | (CH ₂) ₃ Cl | | Et | Et | CH ₂ C(Cl)CH ₂ |
| 15 | Et | Me | (CH ₂) ₃ Cl | | Et | n-Pr | CH ₂ C(Cl)CH ₂ |
| | Et | OCH ₃ | (CH ₂) ₃ Cl | | Et | OCH ₃ | CH ₂ C(Cl)CH ₂ |
| | Et | CH ₂ Ph | (CH ₂) ₃ Cl | | Et | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ |
| | Et | H | c-pentyl | | n-Pr | H | H |
| | Et | Me | c-pentyl | | n-Pr | Me | H |
| 20 | Et | Et | c-pentyl | | n-Pr | Et | H |
| | Et | OCH ₃ | c-pentyl | | n-Pr | n-Pr | H |
| | Et | CH ₂ CHCH ₂ | c-pentyl | | n-Pr | i-Pr | H |
| | Et | CH ₂ CCH | c-pentyl | | n-Pr | n-Bu | H |
| | Et | CH ₂ Ph | c-pentyl | | n-Pr | i-Bu | H |
| 25 | Et | H | c-hexyl | | n-Pr | s-Bu | H |
| | Et | Me | c-hexyl | | n-Pr | t-Bu | H |
| | Et | Et | c-hexyl | | n-Pr | CHO | H |
| | Et | OCH ₃ | c-hexyl | | n-Pr | COCH ₃ | H |
| | Et | CH ₂ CHCH ₂ | c-hexyl | | n-Pr | CH ₂ OCH ₃ | H |

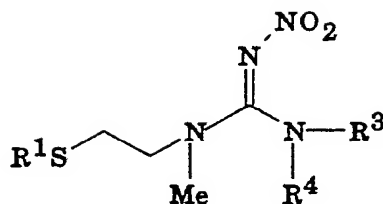
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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|------------------------------------|------------------------------------|--------------------------------------|----------------|
| 5 | n-Pr | OCH ₃ | H | n-Pr | CH ₂ Ph | n-Pr | |
| | n-Pr | SO ₂ CH ₃ | H | | n-Bu | n-Bu | |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | H | | CHO | n-Bu | |
| | n-Pr | CH ₂ CHCH ₂ | H | | SO ₂ CH ₃ | n-Bu | |
| | n-Pr | CH ₂ CCH | H | | CH ₂ CN | n-Bu | |
| 10 | n-Pr | CH ₂ CN | H | n-Pr | CH ₂ Ph | n-Bu | |
| | n-Pr | N(CH ₃) ₂ | H | | Me | c-Pr | |
| | n-Pr | CH ₂ Ph | H | | H | c-Pr | |
| | n-Pr | Me | Me | | H | (CH ₂) ₃ Cl | |
| | n-Pr | CHO | Me | | H | c-pentyl | |
| 15 | n-Pr | COCH ₃ | Me | n-Pr | H | c-hexyl | |
| | n-Pr | OCH ₃ | Me | | H | CH ₂ C(Cl)CH ₂ | |
| | n-Pr | SO ₂ CH ₃ | Me | | H | CH ₂ -c-Pr | |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | Me | | n-Bu | Me | H |
| | n-Pr | CH ₂ CN | Me | | CH ₂ CH ₂ Cl | Me | H |
| 20 | n-Pr | CH ₂ Ph | Me | (CH ₂) ₃ Cl | Me | H | |
| | n-Pr | Et | Et | | (CH ₂) ₄ Cl | Me | H |
| | n-Pr | CHO | Et | | c-Pr | Me | H |
| | n-Pr | COCH ₃ | Et | | c-Bu | Me | H |
| | n-Pr | OCH ₃ | Et | | i-Pr | Me | H |
| 25 | n-Pr | SO ₂ CH ₃ | Et | c-pentyl | Me | H | |
| | n-Pr | CH ₂ CN | Et | | c-hexyl | Me | H |
| | n-Pr | CH ₂ Ph | Et | | CH ₂ -c-Pr | Me | H |
| | n-Pr | i-Pr | i-Pr | | CH ₂ -c-pentyl | Me | H |
| | n-Pr | CHO | n- | | | | |
| 30 | Pr | | | | | | |
| | n-Pr | SO ₂ CH ₃ | n- | | | | |
| | Pr | | | | | | |

TABLE 4

5



| 10 | R ¹ | R ³ | R ⁴ | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|----------------|--|----------------|
| | Me | i-Pr | H | Me | CH ₂ OC(CH ₃) ₂ OCH ₃ | H |
| | Me | n-Bu | H | Me | SO ₂ CH ₃ | H |
| | Me | i-Bu | H | Me | SO ₂ CH ₂ CH ₃ | H |
| 15 | Me | s-Bu | H | Me | SO ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | t-Bu | H | Me | CH ₂ CH ₂ SO ₂ CH ₃ | H |
| | Me | H | H | Me | CH ₂ CHCH ₂ | H |
| | Me | COCH ₃ | H | Me | CH ₂ CH ₂ CHCH ₂ | H |
| | Me | CHO | H | Me | CH ₂ CHCHCH ₃ | H |
| | Me | COCH ₂ CH ₃ | H | Me | CH ₂ CCH | H |
| 20 | Me | CH ₂ OCH ₃ | H | Me | CH ₂ CH ₂ CCH | H |
| | Me | CH ₂ OCH ₂ CH ₃ | H | Me | CH ₂ CCCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ CH ₃ | H | Me | CH ₂ CN | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | H | Me | NHCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₃ | H | Me | NHCH ₂ CH ₃ | H |
| 25 | Me | OCH ₃ | H | Me | NHCH(CH ₃) ₂ | H |
| | Me | OCH ₂ CH ₃ | H | Me | NHC(CH ₃) ₃ | H |
| | Me | OCH ₂ CH ₂ CH ₃ | H | Me | NHCH ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | OCH(CH ₃) ₂ | H | Me | NHCH ₂ CH ₂ CH ₃ | H |
| | Me | CH ₂ OCH(CH ₃)OCH ₃ | H | Me | N(CH ₃) ₂ | H |
| 30 | | | | Me | N(CH ₃)CH ₂ CH ₃ | H |
| | | | | Me | N(CH ₂ CH ₃) ₂ | H |
| | | | | Me | CH ₂ Ph | H |
| | | | | Me | Et | Me |
| 35 | | | | Me | n-Pr | Me |
| | | | | Me | i-Pr | Me |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Me | n-Bu | Me | | Me | OCH ₂ CH ₃ | Et |
| | Me | COCH ₃ | Me | | Me | SO ₂ CH ₃ | Et |
| | Me | CHO | Me | | Me | CH ₂ CH ₂ SO ₂ Me | Et |
| | Me | COCH ₂ CH ₃ | Me | | Me | CH ₂ CHCH ₂ | Et |
| | Me | CH ₂ OCH ₃ | Me | | Me | CH ₂ CCH | Et |
| 10 | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Me | | Me | CH ₂ CN | Et |
| | Me | OCH ₃ | Me | | Me | N(CH ₃) ₂ | Et |
| | Me | OCH ₂ CH ₃ | Me | | Me | n-Pr | n-Pr |
| | Me | SO ₂ CH ₃ | Me | | Me | i-Pr | i-Pr |
| | Me | CH ₂ CH ₂ SO ₂ CH ₃ | Me | | Me | COCH ₃ | n-Pr |
| 15 | Me | CH ₂ CCH | Me | | Me | CHO | n-Pr |
| | Me | CH ₂ CN | Me | | Me | COCH ₂ CH ₃ | n-Pr |
| | Me | NHCH ₃ | Me | | Me | CH ₂ OCH ₃ | n-Pr |
| | Me | N(CH ₃) ₂ | Me | | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Pr |
| | Me | Et | Et | | Me | OCH ₃ | n-Pr |
| 20 | Me | COCH ₃ | Et | | Me | OCH ₂ CH ₃ | n-Pr |
| | Me | CHO | Et | | Me | SO ₂ CH ₃ | n-Pr |
| | Me | COCH ₂ CH ₃ | Et | | Me | CH ₂ CH ₂ SO ₂ CH ₃ | n-Pr |
| | Me | CH ₂ OCH ₃ | Et | | Me | CH ₂ CN | n-Pr |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Et | | Me | N(CH ₃) ₂ | n-Pr |
| 25 | Me | OCH ₃ | Et | | | | |

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| | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|
| 5 | Me | COCH ₃ | n-Bu |
| | Me | CHO | n-Bu |
| | Me | COCH ₂ CH ₃ | n-Bu |
| | Me | CH ₂ OCH ₃ | n-Bu |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Bu |
| 10 | Me | OCH ₃ | n-Bu |
| | Me | SO ₂ CH ₃ | n-Bu |
| | Me | CH ₂ CN | n-Bu |
| | Me | Me | c-Pr |
| | Me | Et | c-Pr |
| 15 | Me | n-Pr | c-Pr |
| | Me | OCH ₃ | c-Pr |
| | Me | CH ₂ CHCH ₂ | c-Pr |
| | Me | CH ₂ CCH | c-Pr |
| | Me | N(CH ₃) ₂ | c-Pr |
| 20 | Me | Me | c-Bu |
| | Me | Et | c-Bu |
| | Me | n-Pr | c-Bu |
| | Me | OCH ₃ | c-Bu |

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| R ¹ | R ³ | R ⁴ |
|----------------|-----------------------------------|------------------------------------|
| Me | CH ₂ CHCH ₂ | c-Bu |
| Me | CH ₂ CCH | c-Bu |
| Me | N(CH ₃) ₂ | c-Bu |
| Me | H | (CH ₂) ₃ Cl |
| Me | Me | (CH ₂) ₃ Cl |
| Me | Et | (CH ₂) ₃ Cl |
| Me | OCH ₃ | (CH ₂) ₃ Cl |
| Me | H | c-pentyl |
| Me | Me | c-pentyl |
| Me | Et | c-pentyl |
| Me | OCH ₃ | c-pentyl |
| Me | CH ₂ CHCH ₂ | c-pentyl |
| Me | CH ₂ CCH | c-pentyl |
| Me | CH ₂ Ph | c-pentyl |
| Me | H | c-hexyl |
| Me | Me | c-hexyl |
| Me | Et | c-hexyl |
| Me | OCH ₃ | c-hexyl |
| Me | CH ₂ CHCH ₂ | c-hexyl |
| Me | CH ₂ CCH | c-hexyl |

| | R ¹ | R ³ | R ⁴ | R ¹ | R ³ | R ⁴ |
|----|----------------|----------------------------------|--------------------------------------|----------------|---|----------------|
| 5 | Me | CH ₂ Ph | CH ₂ -c-Pr | Et | CH ₂ OCH ₃ | H |
| | Me | COCH ₃ | CH ₂ -c-Pr | Et | (CH ₂) ₂ OCH ₂ CH ₃ | H |
| | Me | CHO | CH ₂ -c-Pr | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | H |
| | Me | CH ₂ OCH ₃ | CH ₂ -c-Pr | Et | OCH ₃ | H |
| | Me | SO ₂ CH ₃ | CH ₂ -c-Pr | Et | OCH ₂ CH ₃ | H |
| 10 | Me | CH ₂ CN | CH ₂ -c-Pr | Et | SO ₂ CH ₃ | H |
| | Me | H | CH ₂ C(Cl)CH ₂ | Et | (CH ₂) ₂ SO ₂ CH ₃ | H |
| | Me | Me | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CHCH ₂ | H |
| | Me | Et | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CHCHCH ₃ | H |
| | Me | n-Pr | CH ₂ C(Cl)CH ₂ | Et | (CH ₂) ₂ CHCH ₂ | H |
| 15 | Me | CHO | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CCH | H |
| | Me | OCH ₃ | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CCCH ₃ | H |
| | Me | SO ₂ CH ₃ | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CN | H |
| | Me | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ | Et | NHCH ₃ | H |
| | Et | H | H | Et | N(CH ₃) ₂ | H |
| 20 | Et | Me | H | Et | CH ₂ Ph | H |
| | Et | Et | H | Et | Et | Me |
| | Et | n-Pr | H | Et | n-Pr | Me |
| | Et | i-Pr | H | Et | Me | Me |
| | Et | n-Bu | H | Et | COCH ₃ | Me |
| 25 | Et | i-Bu | H | Et | CHO | Me |
| | Et | s-Bu | H | Et | CH ₂ OCH ₃ | Me |
| | Et | t-Bu | H | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Me |
| | Et | COCH ₃ | H | Et | OCH ₃ | Me |
| | Et | CHO | H | Et | SO ₂ CH ₃ | Me |

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Et | (CH ₂) ₂ SO ₂ CH ₃ | Me | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Pr |
| | Et | CH ₂ CHCH ₂ | Me | | Et | OCH ₃ | n-Pr |
| | Et | CH ₂ CCH | Me | | Et | SO ₂ CH ₃ | n-Pr |
| | Et | CH ₂ CN | Me | | Et | (CH ₂) ₂ SO ₂ CH ₃ | n-Pr |
| | Et | NHCH ₃ | Me | | Et | CH ₂ CHCH ₂ | n-Pr |
| 10 | Et | N(CH ₃) ₂ | Me | | Et | CH ₂ CCH | n-Pr |
| | Et | CH ₂ Ph | Me | | Et | CH ₂ CN | n-Pr |
| | Et | Et | Et | | Et | N(CH ₃) ₂ | n-Pr |
| | Et | COCH ₃ | Et | | Et | CH ₂ Ph | n-Pr |
| | Et | CHO | Et | | Et | n-Bu | n-Bu |
| 15 | Et | CH ₂ OCH ₃ | Et | | Et | CHO | n-Bu |
| | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Et | | Et | COCH ₃ | n-Bu |
| | Et | OCH ₃ | Et | | Et | CH ₂ OCH ₃ | n-Bu |
| | Et | SO ₂ CH ₃ | Et | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Bu |
| | Et | (CH ₂) ₂ SO ₂ CH ₃ | Et | | Et | OCH ₃ | n-Bu |
| 20 | Et | CH ₂ CCH | Et | | Et | SO ₂ CH ₃ | n-Bu |
| | Et | CH ₂ CHCH ₂ | Et | | Et | CH ₂ CN | n-Bu |
| | Et | CH ₂ CN | Et | | Et | CH ₂ Ph | n-Bu |
| | Et | N(CH ₃) ₂ | Et | | Et | i-Pr | i-Pr |
| | Et | CH ₂ Ph | Et | | Et | Me | c-Pr |
| 25 | Et | n-Pr | n-Pr | | Et | Et | c-Pr |
| | Et | CHO | n-Pr | | Et | n-Pr | c-Pr |
| | Et | COCH ₃ | n-Pr | | Et | OCH ₃ | c-Pr |
| | Et | CH ₂ OCH ₃ | n-Pr | | Et | CH ₂ CHCH ₂ | c-Pr |

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|-----------------------------------|------------------------------------|--|----------------|----------------------------------|--------------------------------------|
| 5 | Et | CH ₂ CCH | c-Pr | | Et | CH ₂ CCH | c-hexyl |
| | Et | N(CH ₃) ₂ | c-Pr | | Et | CH ₂ Ph | c-hexyl |
| | Et | CH ₂ Ph | c-Pr | | Et | CH ₂ Ph | CH ₂ -c-Pr |
| | Et | H | c-Pr | | Et | CHO | CH ₂ -c-Pr |
| | Et | H | c-Bu | | Et | CH ₂ OCH ₃ | CH ₂ -c-Pr |
| 10 | Et | Me | c-Bu | | Et | SO ₂ CH ₃ | CH ₂ -c-Pr |
| | Et | OCH ₃ | c-Bu | | Et | CH ₂ CN | CH ₂ -c-Pr |
| | Et | N(CH ₃) ₂ | c-Bu | | Et | H | CH ₂ C(Cl)CH ₂ |
| | Et | CH ₂ Ph | c-Bu | | Et | Me | CH ₂ C(Cl)CH ₂ |
| | Et | H | (CH ₂) ₃ Cl | | Et | Et | CH ₂ C(Cl)CH ₂ |
| 15 | Et | Me | (CH ₂) ₃ Cl | | Et | n-Pr | CH ₂ C(Cl)CH ₂ |
| | Et | OCH ₃ | (CH ₂) ₃ Cl | | Et | OCH ₃ | CH ₂ C(Cl)CH ₂ |
| | Et | CH ₂ Ph | (CH ₂) ₃ Cl | | Et | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ |
| | Et | H | c-pentyl | | n-Pr | H | H |
| | Et | Me | c-pentyl | | n-Pr | Me | H |
| 20 | Et | Et | c-pentyl | | n-Pr | Et | H |
| | Et | OCH ₃ | c-pentyl | | n-Pr | n-Pr | H |
| | Et | CH ₂ CHCH ₂ | c-pentyl | | n-Pr | i-Pr | H |
| | Et | CH ₂ CCH | c-pentyl | | n-Pr | n-Bu | H |
| | Et | CH ₂ Ph | c-pentyl | | n-Pr | i-Bu | H |
| 25 | Et | H | c-hexyl | | n-Pr | s-Bu | H |
| | Et | Me | c-hexyl | | n-Pr | t-Bu | H |
| | Et | Et | c-hexyl | | n-Pr | CHO | H |
| | Et | OCH ₃ | c-hexyl | | n-Pr | COCH ₃ | H |
| | Et | CH ₂ CHCH ₂ | c-hexyl | | n-Pr | CH ₂ OCH ₃ | H |

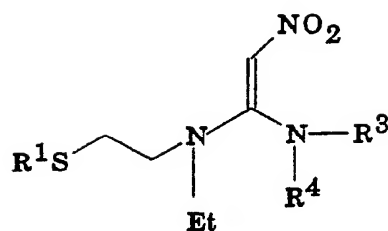
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| | R ¹ | R ³ | R ⁴ | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|------------------------------------|---------------------------------|--------------------------------------|
| 5 | n-Pr | OCH ₃ | H | n-Pr | CH ₂ Ph | n-Pr |
| | n-Pr | SO ₂ CH ₃ | H | n-Pr | n-Bu | n-Bu |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | H | n-Pr | CHO | n-Bu |
| | n-Pr | CH ₂ CHCH ₂ | H | n-Pr | SO ₂ CH ₃ | n-Bu |
| | n-Pr | CH ₂ CCH | H | n-Pr | CH ₂ CN | n-Bu |
| 10 | n-Pr | CH ₂ CN | H | n-Pr | CH ₂ Ph | n-Bu |
| | n-Pr | N(CH ₃) ₂ | H | n-Pr | Me | c-Pr |
| | n-Pr | CH ₂ Ph | H | n-Pr | H | c-Pr |
| | n-Pr | Me | Me | n-Pr | H | (CH ₂) ₃ Cl |
| | n-Pr | CHO | Me | n-Pr | H | c-pentyl |
| 15 | n-Pr | COCH ₃ | Me | n-Pr | H | c-hexyl |
| | n-Pr | OCH ₃ | Me | n-Pr | H | CH ₂ C(Cl)CH ₂ |
| | n-Pr | SO ₂ CH ₃ | Me | n-Pr | H | CH ₂ -c-Pr |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | Me | n-Bu | Me | H |
| | n-Pr | CH ₂ CN | Me | CH ₂ CH ₂ Cl | Me | H |
| 20 | n-Pr | CH ₂ Ph | Me | (CH ₂) ₃ Cl | Me | H |
| | n-Pr | Et | Et | (CH ₂) ₄ Cl | Me | H |
| | n-Pr | CHO | Et | c-Pr | Me | H |
| | n-Pr | COCH ₃ | Et | c-Bu | Me | H |
| | n-Pr | OCH ₃ | Et | i-Pr | Me | H |
| 25 | n-Pr | SO ₂ CH ₃ | Et | c-pentyl | Me | H |
| | n-Pr | CH ₂ CN | Et | c-hexyl | Me | H |
| | n-Pr | CH ₂ Ph | Et | CH ₂ -c-Pr | Me | H |
| | n-Pr | i-Pr | i-Pr | CH ₂ -c-pentyl | Me | H |
| | n-Pr | CHO | n- | | | |
| 30 | Pr | | | | | |
| | n-Pr | SO ₂ CH ₃ | n- | | | |
| | Pr | | | | | |

TABLE 5

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| 10 | R ¹ | R ³ | R ⁴ | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|----------------|--|----------------|
| | Me | i-Pr | H | Me | CH ₂ OC(CH ₃) ₂ OCH ₃ | H |
| | Me | n-Bu | H | Me | SO ₂ CH ₃ | H |
| | Me | i-Bu | H | Me | SO ₂ CH ₂ CH ₃ | H |
| 15 | Me | s-Bu | H | Me | SO ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | t-Bu | H | Me | CH ₂ CH ₂ SO ₂ CH ₃ | H |
| | Me | H | H | Me | CH ₂ CHCH ₂ | H |
| | Me | COCH ₃ | H | Me | CH ₂ CH ₂ CHCH ₂ | H |
| | Me | CHO | H | Me | CH ₂ CHCHCH ₃ | H |
| 20 | Me | COCH ₂ CH ₃ | H | Me | CH ₂ CCH | H |
| | Me | CH ₂ OCH ₃ | H | Me | CH ₂ CH ₂ CCH | H |
| | Me | CH ₂ OCH ₂ CH ₃ | H | Me | CH ₂ CCCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ CH ₃ | H | Me | CH ₂ CN | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | H | Me | NHCH ₃ | H |
| 25 | Me | CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₃ | H | Me | NHCH ₂ CH ₃ | H |
| | Me | OCH ₃ | H | Me | NHCH(CH ₃) ₂ | H |
| | Me | OCH ₂ CH ₃ | H | Me | NHC(CH ₃) ₃ | H |
| | Me | OCH ₂ CH ₂ CH ₃ | H | Me | NHCH ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | OCH(CH ₃) ₂ | H | Me | NHCH ₂ CH ₂ CH ₃ | H |
| 30 | Me | CH ₂ OCH(CH ₃)OCH ₃ | H | Me | N(CH ₃) ₂ | H |

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Me | N(CH ₃)CH ₂ CH ₃ | H | | Me | CH ₂ OCH ₃ | Et |
| | Me | N(CH ₂ CH ₃) ₂ | H | | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Et |
| | Me | CH ₂ Ph | H | | Me | OCH ₃ | Et |
| | Me | Et | Me | | Me | OCH ₂ CH ₃ | Et |
| | Me | n-Pr | Me | | Me | SO ₂ CH ₃ | Et |
| 10 | Me | i-Pr | Me | | Me | CH ₂ CH ₂ SO ₂ Me | Et |
| | Me | n-Bu | Me | | Me | CH ₂ CHCH ₂ | Et |
| | Me | COCH ₃ | Me | | Me | CH ₂ CCH | Et |
| | Me | CHO | Me | | Me | CH ₂ CN | Et |
| | Me | COCH ₂ CH ₃ | Me | | Me | N(CH ₃) ₂ | Et |
| 15 | Me | CH ₂ OCH ₃ | Me | | Me | n-Pr | n-Pr |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Me | | Me | i-Pr | i-Pr |
| | Me | OCH ₃ | Me | | Me | COCH ₃ | n-Pr |
| | Me | OCH ₂ CH ₃ | Me | | Me | CHO | n-Pr |
| | Me | SO ₂ CH ₃ | Me | | Me | COCH ₂ CH ₃ | n-Pr |
| 20 | Me | CH ₂ CH ₂ SO ₂ CH ₃ | Me | | Me | CH ₂ OCH ₃ | n-Pr |
| | Me | CH ₂ CCH | Me | | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Pr |
| | Me | CH ₂ CN | Me | | Me | OCH ₃ | n-Pr |
| | Me | NHCH ₃ | Me | | Me | OCH ₂ CH ₃ | n-Pr |
| | Me | N(CH ₃) ₂ | Me | | Me | SO ₂ CH ₃ | n-Pr |
| 25 | Me | Et | Et | | Me | CH ₂ CH ₂ SO ₂ CH ₃ | n-Pr |
| | Me | COCH ₃ | Et | | Me | CH ₂ CN | n-Pr |
| | Me | CHO | Et | | Me | N(CH ₃) ₂ | n-Pr |
| | Me | COCH ₂ CH ₃ | Et | | | | |

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| | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|
| 5 | Me | COCH ₃ | n-Bu |
| | Me | CHO | n-Bu |
| | Me | COCH ₂ CH ₃ | n-Bu |
| | Me | CH ₂ OCH ₃ | n-Bu |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Bu |
| 10 | Me | OCH ₃ | n-Bu |
| | Me | SO ₂ CH ₃ | n-Bu |
| | Me | CH ₂ CN | n-Bu |
| | Me | Me | c-Pr |
| | Me | Et | c-Pr |
| 15 | Me | n-Pr | c-Pr |
| | Me | OCH ₃ | c-Pr |
| | Me | CH ₂ CHCH ₂ | c-Pr |
| | Me | CH ₂ CCH | c-Pr |
| | Me | N(CH ₃) ₂ | c-Pr |
| 20 | Me | Me | c-Bu |
| | Me | Et | c-Bu |
| | Me | n-Pr | c-Bu |
| | Me | OCH ₃ | c-Bu |

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| R ¹ | R ³ | R ⁴ |
|----------------|-----------------------------------|------------------------------------|
| Me | CH ₂ CHCH ₂ | c-Bu |
| Me | CH ₂ CCH | c-Bu |
| Me | N(CH ₃) ₂ | c-Bu |
| Me | H | (CH ₂) ₃ Cl |
| Me | Me | (CH ₂) ₃ Cl |
| Me | Et | (CH ₂) ₃ Cl |
| Me | OCH ₃ | (CH ₂) ₃ Cl |
| Me | H | c-pentyl |
| Me | Me | c-pentyl |
| Me | Et | c-pentyl |
| Me | OCH ₃ | c-pentyl |
| Me | CH ₂ CHCH ₂ | c-pentyl |
| Me | CH ₂ CCH | c-pentyl |
| Me | CH ₂ Ph | c-pentyl |
| Me | H | c-hexyl |
| Me | Me | c-hexyl |
| Me | Et | c-hexyl |
| Me | OCH ₃ | c-hexyl |
| Me | CH ₂ CHCH ₂ | c-hexyl |
| Me | CH ₂ CCH | c-hexyl |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|----------------------------------|--------------------------------------|----|---|----------------|----------------|
| 5 | Me | CH ₂ Ph | CH ₂ -c-Pr | Et | CH ₂ OCH ₃ | H | |
| | Me | COCH ₃ | CH ₂ -c-Pr | Et | (CH ₂) ₂ OCH ₂ CH ₃ | H | |
| | Me | CHO | CH ₂ -c-Pr | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | H | |
| | Me | CH ₂ OCH ₃ | CH ₂ -c-Pr | Et | OCH ₃ | H | |
| | Me | SO ₂ CH ₃ | CH ₂ -c-Pr | Et | OCH ₂ CH ₃ | H | |
| 10 | Me | CH ₂ CN | CH ₂ -c-Pr | Et | SO ₂ CH ₃ | H | |
| | Me | H | CH ₂ C(Cl)CH ₂ | Et | (CH ₂) ₂ SO ₂ CH ₃ | H | |
| | Me | Me | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CHCH ₂ | H | |
| | Me | Et | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CHCHCH ₃ | H | |
| | Me | n-Pr | CH ₂ C(Cl)CH ₂ | Et | (CH ₂) ₂ CHCH ₂ | H | |
| 15 | Me | CHO | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CCH | H | |
| | Me | OCH ₃ | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CCCH ₃ | H | |
| | Me | SO ₂ CH ₃ | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CN | H | |
| | Me | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ | Et | NHCH ₃ | H | |
| | Et | H | H | Et | N(CH ₃) ₂ | H | |
| 20 | Et | Me | H | Et | CH ₂ Ph | H | |
| | Et | Et | H | Et | Et | Me | |
| | Et | n-Pr | H | Et | n-Pr | Me | |
| | Et | i-Pr | H | Et | Me | Me | |
| | Et | n-Bu | H | Et | COCH ₃ | Me | |
| 25 | Et | i-Bu | H | Et | CHO | Me | |
| | Et | s-Bu | H | Et | CH ₂ OCH ₃ | Me | |
| | Et | t-Bu | H | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Me | |
| | Et | COCH ₃ | H | Et | OCH ₃ | Me | |
| | Et | CHO | H | Et | SO ₂ CH ₃ | Me | |
| 30 | | | | | | | |
| 35 | | | | | | | |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Et | (CH ₂) ₂ SO ₂ CH ₃ | Me | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Pr |
| | Et | CH ₂ CHCH ₂ | Me | | Et | OCH ₃ | n-Pr |
| | Et | CH ₂ CCH | Me | | Et | SO ₂ CH ₃ | n-Pr |
| | Et | CH ₂ CN | Me | | Et | (CH ₂) ₂ SO ₂ CH ₃ | n-Pr |
| | Et | NHCH ₃ | Me | | Et | CH ₂ CHCH ₂ | n-Pr |
| 10 | Et | N(CH ₃) ₂ | Me | | Et | CH ₂ CCH | n-Pr |
| | Et | CH ₂ Ph | Me | | Et | CH ₂ CN | n-Pr |
| | Et | Et | Et | | Et | N(CH ₃) ₂ | n-Pr |
| | Et | COCH ₃ | Et | | Et | CH ₂ Ph | n-Pr |
| | Et | CHO | Et | | Et | n-Bu | n-Bu |
| 15 | Et | CH ₂ OCH ₃ | Et | | Et | CHO | n-Bu |
| | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Et | | Et | COCH ₃ | n-Bu |
| | Et | OCH ₃ | Et | | Et | CH ₂ OCH ₃ | n-Bu |
| | Et | SO ₂ CH ₃ | Et | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Bu |
| | Et | (CH ₂) ₂ SO ₂ CH ₃ | Et | | Et | OCH ₃ | n-Bu |
| 20 | Et | CH ₂ CCH | Et | | Et | SO ₂ CH ₃ | n-Bu |
| | Et | CH ₂ CHCH ₂ | Et | | Et | CH ₂ CN | n-Bu |
| | Et | CH ₂ CN | Et | | Et | CH ₂ Ph | n-Bu |
| | Et | N(CH ₃) ₂ | Et | | Et | i-Pr | i-Pr |
| | Et | CH ₂ Ph | Et | | Et | Me | c-Pr |
| 25 | Et | n-Pr | n-Pr | | Et | Et | c-Pr |
| | Et | CHO | n-Pr | | Et | n-Pr | c-Pr |
| | Et | COCH ₃ | n-Pr | | Et | OCH ₃ | c-Pr |
| | Et | CH ₂ OCH ₃ | n-Pr | | Et | CH ₂ CHCH ₂ | c-Pr |

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| | R ¹ | R ³ | R ⁴ |
|----|----------------|-----------------------------------|------------------------------------|
| 5 | Et | CH ₂ CCH | c-Pr |
| | Et | N(CH ₃) ₂ | c-Pr |
| | Et | CH ₂ Ph | c-Pr |
| | Et | H | c-Pr |
| | Et | H | c-Bu |
| 10 | Et | Me | c-Bu |
| | Et | OCH ₃ | c-Bu |
| | Et | N(CH ₃) ₂ | c-Bu |
| | Et | CH ₂ Ph | c-Bu |
| | Et | H | (CH ₂) ₃ Cl |
| 15 | Et | Me | (CH ₂) ₃ Cl |
| | Et | OCH ₃ | (CH ₂) ₃ Cl |
| | Et | CH ₂ Ph | (CH ₂) ₃ Cl |
| | Et | H | c-pentyl |
| | Et | Me | c-pentyl |
| 20 | Et | Et | c-pentyl |
| | Et | OCH ₃ | c-pentyl |
| | Et | CH ₂ CHCH ₂ | c-pentyl |
| | Et | CH ₂ CCH | c-pentyl |
| | Et | CH ₂ Ph | c-pentyl |
| 25 | Et | H | c-hexyl |
| | Et | Me | c-hexyl |
| | Et | Et | c-hexyl |
| | Et | OCH ₃ | c-hexyl |
| | Et | CH ₂ CHCH ₂ | c-hexyl |

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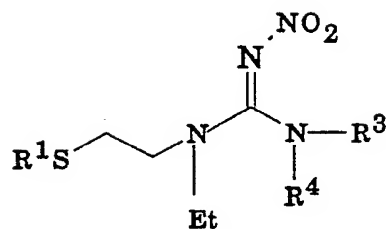
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| R ¹ | R ³ | R ⁴ |
|----------------|----------------------------------|--------------------------------------|
| Et | CH ₂ CCH | c-hexyl |
| Et | CH ₂ Ph | c-hexyl |
| Et | CH ₂ Ph | CH ₂ -c-Pr |
| Et | CHO | CH ₂ -c-Pr |
| Et | CH ₂ OCH ₃ | CH ₂ -c-Pr |
| Et | SO ₂ CH ₃ | CH ₂ -c-Pr |
| Et | CH ₂ CN | CH ₂ -c-Pr |
| Et | H | CH ₂ C(Cl)CH ₂ |
| Et | Me | CH ₂ C(Cl)CH ₂ |
| Et | Et | CH ₂ C(Cl)CH ₂ |
| Et | n-Pr | CH ₂ C(Cl)CH ₂ |
| Et | OCH ₃ | CH ₂ C(Cl)CH ₂ |
| Et | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ |
| n-Pr | H | H |
| n-Pr | Me | H |
| n-Pr | Et | H |
| n-Pr | n-Pr | H |
| n-Pr | i-Pr | H |
| n-Pr | n-Bu | H |
| n-Pr | i-Bu | H |
| n-Pr | s-Bu | H |
| n-Pr | t-Bu | H |
| n-Pr | CHO | H |
| n-Pr | COCH ₃ | H |
| n-Pr | CH ₂ OCH ₃ | H |

| | R ¹ | R ³ | R ⁴ | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|------------------------------------|---------------------------------|--------------------------------------|
| 5 | n-Pr | OCH ₃ | H | n-Pr | CH ₂ Ph | n-Pr |
| | n-Pr | SO ₂ CH ₃ | H | n-Pr | n-Bu | n-Bu |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | H | n-Pr | CHO | n-Bu |
| | n-Pr | CH ₂ CHCH ₂ | H | n-Pr | SO ₂ CH ₃ | n-Bu |
| | n-Pr | CH ₂ CCH | H | n-Pr | CH ₂ CN | n-Bu |
| 10 | n-Pr | CH ₂ CN | H | n-Pr | CH ₂ Ph | n-Bu |
| | n-Pr | N(CH ₃) ₂ | H | n-Pr | Me | c-Pr |
| | n-Pr | CH ₂ Ph | H | n-Pr | H | c-Pr |
| | n-Pr | Me | Me | n-Pr | H | (CH ₂) ₃ Cl |
| | n-Pr | CHO | Me | n-Pr | H | c-pentyl |
| 15 | n-Pr | COCH ₃ | Me | n-Pr | H | c-hexyl |
| | n-Pr | OCH ₃ | Me | n-Pr | H | CH ₂ C(Cl)CH ₂ |
| | n-Pr | SO ₂ CH ₃ | Me | n-Pr | H | CH ₂ -c-Pr |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | Me | n-Bu | Me | H |
| | n-Pr | CH ₂ CN | Me | CH ₂ CH ₂ Cl | Me | H |
| 20 | n-Pr | CH ₂ Ph | Me | (CH ₂) ₃ Cl | Me | H |
| | n-Pr | Et | Et | (CH ₂) ₄ Cl | Me | H |
| | n-Pr | CHO | Et | c-Pr | Me | H |
| | n-Pr | COCH ₃ | Et | c-Bu | Me | H |
| | n-Pr | OCH ₃ | Et | i-Pr | Me | H |
| 25 | n-Pr | SO ₂ CH ₃ | Et | c-pentyl | Me | H |
| | n-Pr | CH ₂ CN | Et | c-hexyl | Me | H |
| | n-Pr | CH ₂ Ph | Et | CH ₂ -c-Pr | Me | H |
| | n-Pr | i-Pr | i-Pr | CH ₂ -c-pentyl | Me | H |
| | n-Pr | CHO | n- | | | |
| 30 | Pr | | | | | |
| | n-Pr | SO ₂ CH ₃ | n- | | | |
| | Pr | | | | | |

TABLE 6

5



| 10 | R ¹ | R ³ | R ⁴ | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|----------------|---|----------------|
| | Me | i-Pr | H | Me | SO ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | n-Bu | H | Me | CH ₂ CH ₂ SO ₂ CH ₃ | H |
| | Me | i-Bu | H | Me | CH ₂ CHCH ₂ | H |
| 15 | Me | s-Bu | H | Me | CH ₂ CH ₂ CHCH ₂ | H |
| | Me | t-Bu | H | Me | CH ₂ CHCHCH ₃ | H |
| | Me | H | H | Me | CH ₂ CCH | H |
| | Me | COCH ₃ | H | Me | CH ₂ CH ₂ CCH | H |
| | Me | CHO | H | Me | CH ₂ CCCH ₃ | H |
| 20 | Me | COCH ₂ CH ₃ | H | Me | CH ₂ CN | H |
| | Me | CH ₂ OCH ₃ | H | Me | NHCH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₃ | H | Me | NHCH ₂ CH ₃ | H |
| | Me | CH ₂ OCH ₂ CH ₂ CH ₃ | H | Me | NHCH(CH ₃) ₂ | H |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | H | Me | NHC(CH ₃) ₃ | H |
| 25 | Me | CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₃ | H | Me | NHCH ₂ CH ₂ CH ₂ CH ₃ | H |
| | Me | OCH ₃ | H | Me | NHCH ₂ CH ₂ CH ₃ | H |
| | Me | OCH ₂ CH ₃ | H | Me | N(CH ₃) ₂ | H |
| | Me | OCH ₂ CH ₂ CH ₃ | H | Me | N(CH ₃)CH ₂ CH ₃ | H |
| | Me | OCH(CH ₃) ₂ | H | Me | N(CH ₂ CH ₃) ₂ | H |
| 30 | Me | CH ₂ OCH(CH ₃)OCH ₃ | H | Me | CH ₂ Ph | H |
| | Me | CH ₂ OC(CH ₃) ₂ OCH ₃ | H | Me | Et | Me |
| | Me | SO ₂ CH ₃ | H | Me | n-Pr | Me |
| | Me | SO ₂ CH ₂ CH ₃ | H | Me | i-Pr | Me |

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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Me | n-Bu | Me | | Me | OCH ₂ CH ₃ | Et |
| | Me | COCH ₃ | Me | | Me | SO ₂ CH ₃ | Et |
| | Me | CHO | Me | | Me | CH ₂ CH ₂ SO ₂ Me | Et |
| | Me | COCH ₂ CH ₃ | Me | | Me | CH ₂ CHCH ₂ | Et |
| | Me | CH ₂ OCH ₃ | Me | | Me | CH ₂ CCH | Et |
| 10 | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Me | | Me | CH ₂ CN | Et |
| | Me | OCH ₃ | Me | | Me | N(CH ₃) ₂ | Et |
| | Me | OCH ₂ CH ₃ | Me | | Me | n-Pr | n-Pr |
| | Me | SO ₂ CH ₃ | Me | | Me | i-Pr | i-Pr |
| | Me | CH ₂ CH ₂ SO ₂ CH ₃ | Me | | Me | COCH ₃ | n-Pr |
| 15 | Me | CH ₂ CCH | Me | | Me | CHO | n-Pr |
| | Me | CH ₂ CN | Me | | Me | COCH ₂ CH ₃ | n-Pr |
| | Me | NHCH ₃ | Me | | Me | CH ₂ OCH ₃ | n-Pr |
| | Me | N(CH ₃) ₂ | Me | | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Pr |
| | Me | Et | Et | | Me | OCH ₃ | n-Pr |
| 20 | Me | COCH ₃ | Et | | Me | OCH ₂ CH ₃ | n-Pr |
| | Me | CHO | Et | | Me | SO ₂ CH ₃ | n-Pr |
| | Me | COCH ₂ CH ₃ | Et | | Me | CH ₂ CH ₂ SO ₂ CH ₃ | n-Pr |
| | Me | CH ₂ OCH ₃ | Et | | Me | CH ₂ CN | n-Pr |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | Et | | Me | N(CH ₃) ₂ | n-Pr |
| 25 | Me | OCH ₃ | Et | | | | |

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| | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|
| 5 | Me | COCH ₃ | n-Bu |
| | Me | CHO | n-Bu |
| | Me | COCH ₂ CH ₃ | n-Bu |
| | Me | CH ₂ OCH ₃ | n-Bu |
| | Me | CH ₂ OCH ₂ CH ₂ OCH ₃ | n-Bu |
| 10 | Me | OCH ₃ | n-Bu |
| | Me | SO ₂ CH ₃ | n-Bu |
| | Me | CH ₂ CN | n-Bu |
| | Me | Me | c-Pr |
| | Me | Et | c-Pr |
| 15 | Me | n-Pr | c-Pr |
| | Me | OCH ₃ | c-Pr |
| | Me | CH ₂ CHCH ₂ | c-Pr |
| | Me | CH ₂ CCH | c-Pr |
| | Me | N(CH ₃) ₂ | c-Pr |
| 20 | Me | Me | c-Bu |
| | Me | Et | c-Bu |
| | Me | n-Pr | c-Bu |
| | Me | OCH ₃ | c-Bu |

25

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| R ¹ | R ³ | R ⁴ |
|----------------|-----------------------------------|------------------------------------|
| Me | CH ₂ CHCH ₂ | c-Bu |
| Me | CH ₂ CCH | c-Bu |
| Me | N(CH ₃) ₂ | c-Bu |
| Me | H | (CH ₂) ₃ Cl |
| Me | Me | (CH ₂) ₃ Cl |
| Me | Et | (CH ₂) ₃ Cl |
| Me | OCH ₃ | (CH ₂) ₃ Cl |
| Me | H | c-pentyl |
| Me | Me | c-pentyl |
| Me | Et | c-pentyl |
| Me | OCH ₃ | c-pentyl |
| Me | CH ₂ CHCH ₂ | c-pentyl |
| Me | CH ₂ CCH | c-pentyl |
| Me | CH ₂ Ph | c-pentyl |
| Me | H | c-hexyl |
| Me | Me | c-hexyl |
| Me | Et | c-hexyl |
| Me | OCH ₃ | c-hexyl |
| Me | CH ₂ CHCH ₂ | c-hexyl |
| Me | CH ₂ CCH | c-hexyl |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|----------------------------------|--------------------------------------|----|---|----------------|----------------|
| 5 | Me | CH ₂ Ph | CH ₂ -c-Pr | Et | CH ₂ OCH ₃ | H | |
| | Me | COCH ₃ | CH ₂ -c-Pr | Et | (CH ₂) ₂ OCH ₂ CH ₃ | H | |
| | Me | CHO | CH ₂ -c-Pr | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | H | |
| | Me | CH ₂ OCH ₃ | CH ₂ -c-Pr | Et | OCH ₃ | H | |
| | Me | SO ₂ CH ₃ | CH ₂ -c-Pr | Et | OCH ₂ CH ₃ | H | |
| 10 | Me | CH ₂ CN | CH ₂ -c-Pr | Et | SO ₂ CH ₃ | H | |
| | Me | H | CH ₂ C(Cl)CH ₂ | Et | (CH ₂) ₂ SO ₂ CH ₃ | H | |
| | Me | Me | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CHCH ₂ | H | |
| | Me | Et | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CHCHCH ₃ | H | |
| | Me | n-Pr | CH ₂ C(Cl)CH ₂ | Et | (CH ₂) ₂ CHCH ₂ | H | |
| 15 | Me | CHO | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CCH | H | |
| | Me | OCH ₃ | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CCCH ₃ | H | |
| | Me | SO ₂ CH ₃ | CH ₂ C(Cl)CH ₂ | Et | CH ₂ CN | H | |
| | Me | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ | Et | NHCH ₃ | H | |
| | Et | H | H | Et | N(CH ₃) ₂ | H | |
| 20 | Et | Me | H | Et | CH ₂ Ph | H | |
| | Et | Et | H | Et | Et | Me | |
| | Et | n-Pr | H | Et | n-Pr | Me | |
| | Et | i-Pr | H | Et | Me | Me | |
| | Et | n-Bu | H | Et | COCH ₃ | Me | |
| 25 | Et | i-Bu | H | Et | CHO | Me | |
| | Et | s-Bu | H | Et | CH ₂ OCH ₃ | Me | |
| | Et | t-Bu | H | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Me | |
| | Et | COCH ₃ | H | Et | OCH ₃ | Me | |
| | Et | CHO | H | Et | SO ₂ CH ₃ | Me | |
| 30 | | | | | | | |
| 35 | | | | | | | |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|--|----------------|---|----------------|
| 5 | Et | (CH ₂) ₂ SO ₂ CH ₃ | Me | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Pr |
| | Et | CH ₂ CHCH ₂ | Me | | Et | OCH ₃ | n-Pr |
| | Et | CH ₂ CCH | Me | | Et | SO ₂ CH ₃ | n-Pr |
| | Et | CH ₂ CN | Me | | Et | (CH ₂) ₂ SO ₂ CH ₃ | n-Pr |
| | Et | NHCH ₃ | Me | | Et | CH ₂ CHCH ₂ | n-Pr |
| 10 | Et | N(CH ₃) ₂ | Me | | Et | CH ₂ CCH | n-Pr |
| | Et | CH ₂ Ph | Me | | Et | CH ₂ CN | n-Pr |
| | Et | Et | Et | | Et | N(CH ₃) ₂ | n-Pr |
| | Et | COCH ₃ | Et | | Et | CH ₂ Ph | n-Pr |
| 15 | Et | CHO | Et | | Et | n-Bu | n-Bu |
| | Et | CH ₂ OCH ₃ | Et | | Et | CHO | n-Bu |
| | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | Et | | Et | COCH ₃ | n-Bu |
| | Et | OCH ₃ | Et | | Et | CH ₂ OCH ₃ | n-Bu |
| | Et | SO ₂ CH ₃ | Et | | Et | CH ₂ O(CH ₂) ₂ OCH ₃ | n-Bu |
| | Et | (CH ₂) ₂ SO ₂ CH ₃ | Et | | Et | OCH ₃ | n-Bu |
| 20 | Et | CH ₂ CCH | Et | | Et | SO ₂ CH ₃ | n-Bu |
| | Et | CH ₂ CHCH ₂ | Et | | Et | CH ₂ CN | n-Bu |
| | Et | CH ₂ CN | Et | | Et | CH ₂ Ph | n-Bu |
| | Et | N(CH ₃) ₂ | Et | | Et | i-Pr | i-Pr |
| | Et | CH ₂ Ph | Et | | Et | Me | c-Pr |
| 25 | Et | n-Pr | n-Pr | | Et | Et | c-Pr |
| | Et | CHO | n-Pr | | Et | n-Pr | c-Pr |
| | Et | COCH ₃ | n-Pr | | Et | OCH ₃ | c-Pr |
| | Et | CH ₂ OCH ₃ | n-Pr | | Et | CH ₂ CHCH ₂ | c-Pr |
| 30 | | | | | | | |
| 35 | | | | | | | |

| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|-----------------------------------|------------------------------------|--|----------------|----------------------------------|--------------------------------------|
| 5 | Et | CH ₂ CCH | c-Pr | | Et | CH ₂ CCH | c-hexyl |
| | Et | N(CH ₃) ₂ | c-Pr | | Et | CH ₂ Ph | c-hexyl |
| | Et | CH ₂ Ph | c-Pr | | Et | CH ₂ Ph | CH ₂ -c-Pr |
| | Et | H | c-Pr | | Et | CHO | CH ₂ -c-Pr |
| | Et | H | c-Bu | | Et | CH ₂ OCH ₃ | CH ₂ -c-Pr |
| 10 | Et | Me | c-Bu | | Et | SO ₂ CH ₃ | CH ₂ -c-Pr |
| | Et | OCH ₃ | c-Bu | | Et | CH ₂ CN | CH ₂ -c-Pr |
| | Et | N(CH ₃) ₂ | c-Bu | | Et | H | CH ₂ C(Cl)CH ₂ |
| | Et | CH ₂ Ph | c-Bu | | Et | Me | CH ₂ C(Cl)CH ₂ |
| | Et | H | (CH ₂) ₃ Cl | | Et | Et | CH ₂ C(Cl)CH ₂ |
| 15 | Et | Me | (CH ₂) ₃ Cl | | Et | n-Pr | CH ₂ C(Cl)CH ₂ |
| | Et | OCH ₃ | (CH ₂) ₃ Cl | | Et | OCH ₃ | CH ₂ C(Cl)CH ₂ |
| | Et | CH ₂ Ph | (CH ₂) ₃ Cl | | Et | N(CH ₃) ₂ | CH ₂ C(Cl)CH ₂ |
| | Et | H | c-pentyl | | n-Pr | H | H |
| | Et | Me | c-pentyl | | n-Pr | Me | H |
| 20 | Et | Et | c-pentyl | | n-Pr | Et | H |
| | Et | OCH ₃ | c-pentyl | | n-Pr | n-Pr | H |
| | Et | CH ₂ CHCH ₂ | c-pentyl | | n-Pr | i-Pr | H |
| | Et | CH ₂ CCH | c-pentyl | | n-Pr | n-Bu | H |
| | Et | CH ₂ Ph | c-pentyl | | n-Pr | i-Bu | H |
| 25 | Et | H | c-hexyl | | n-Pr | s-Bu | H |
| | Et | Me | c-hexyl | | n-Pr | t-Bu | H |
| | Et | Et | c-hexyl | | n-Pr | CHO | H |
| | Et | OCH ₃ | c-hexyl | | n-Pr | COCH ₃ | H |
| | Et | CH ₂ CHCH ₂ | c-hexyl | | n-Pr | CH ₂ OCH ₃ | H |

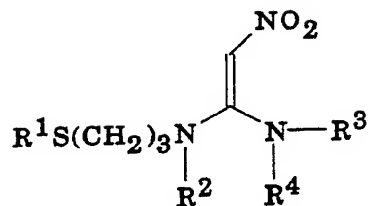
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| | R ¹ | R ³ | R ⁴ | | R ¹ | R ³ | R ⁴ |
|----|----------------|---|----------------|------------------------------------|---------------------------------|--------------------------------------|----------------|
| 5 | n-Pr | OCH ₃ | H | n-Pr | CH ₂ Ph | n-Pr | |
| | n-Pr | SO ₂ CH ₃ | H | n-Pr | n-Bu | n-Bu | |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | H | n-Pr | CHO | n-Bu | |
| | n-Pr | CH ₂ CHCH ₂ | H | n-Pr | SO ₂ CH ₃ | n-Bu | |
| | n-Pr | CH ₂ CCH | H | n-Pr | CH ₂ CN | n-Bu | |
| 10 | n-Pr | CH ₂ CN | H | n-Pr | CH ₂ Ph | n-Bu | |
| | n-Pr | N(CH ₃) ₂ | H | n-Pr | Me | c-Pr | |
| | n-Pr | CH ₂ Ph | H | n-Pr | H | c-Pr | |
| | n-Pr | Me | Me | n-Pr | H | (CH ₂) ₃ Cl | |
| | n-Pr | CHO | Me | n-Pr | H | c-pentyl | |
| 15 | n-Pr | COCH ₃ | Me | n-Pr | H | c-hexyl | |
| | n-Pr | OCH ₃ | Me | n-Pr | H | CH ₂ C(Cl)CH ₂ | |
| | n-Pr | SO ₂ CH ₃ | Me | n-Pr | H | CH ₂ -c-Pr | |
| | n-Pr | (CH ₂) ₂ SO ₂ CH ₃ | Me | n-Bu | Me | H | |
| | n-Pr | CH ₂ CN | Me | CH ₂ CH ₂ Cl | Me | H | |
| 20 | n-Pr | CH ₂ Ph | Me | (CH ₂) ₃ Cl | Me | H | |
| | n-Pr | Et | Et | (CH ₂) ₄ Cl | Me | H | |
| | n-Pr | CHO | Et | c-Pr | Me | H | |
| | n-Pr | COCH ₃ | Et | c-Bu | Me | H | |
| | n-Pr | OCH ₃ | Et | i-Pr | Me | H | |
| 25 | n-Pr | SO ₂ CH ₃ | Et | c-pentyl | Me | H | |
| | n-Pr | CH ₂ CN | Et | c-hexyl | Me | H | |
| | n-Pr | CH ₂ Ph | Et | CH ₂ -c-Pr | Me | H | |
| | n-Pr | i-Pr | i-Pr | CH ₂ -c-pentyl | Me | H | |
| | n-Pr | CHO | n- | | | | |
| 30 | Pr | | | | | | |
| | n-Pr | SO ₂ CH ₃ | n- | | | | |
| | Pr | | | | | | |

TABLE 7

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| | R ¹ | R ² | R ³ | R ⁴ | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|----------------------------------|----------------|----------------|----------------|----------------------------------|----------------|----------------|
| 10 | Me | H | Me | H | Me | Et | Et | H |
| | Me | Me | Me | H | Me | n-Pr | Et | H |
| | Me | Et | Me | H | Me | CHO | Et | H |
| | Me | n-Pr | Me | H | Me | CH ₂ CN | Et | H |
| 15 | Me | CHO | Me | H | Me | COCH ₃ | Et | H |
| | Me | CH ₂ CN | Me | H | Me | CH ₂ NMe ₂ | Et | H |
| | Me | COCH ₃ | Me | H | Et | H | Me | H |
| | Me | CH ₂ NMe ₂ | Me | H | Et | Me | Me | H |
| 20 | Me | H | Me | Me | Et | CHO | Me | H |
| | Me | Me | Me | Me | Et | CH ₂ CN | Me | H |
| | Me | Et | Me | Me | Et | H | Me | Me |
| | Me | n-Pr | Me | Me | Et | Me | Me | Me |
| | Me | CHO | Me | Me | Et | CHO | Me | Me |
| | Me | CH ₂ CN | Me | Me | Et | CH ₂ CN | Me | Me |
| 25 | Me | COCH ₃ | Me | Me | Et | H | Et | H |
| | Me | CH ₂ NMe ₂ | Me | Me | Et | Me | Et | H |
| | Me | H | Et | H | Et | CHO | Et | H |
| | Me | Me | Et | H | Et | CH ₂ CN | Et | H |

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TABLE 8

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$$\begin{array}{c}
 \text{N} - \text{NO}_2 \\
 \parallel \\
 \text{R}^1\text{S}(\text{CH}_2)_3\text{N} \begin{array}{c} \diagup \\ \text{R}^2 \end{array} \text{C} \begin{array}{c} \diagdown \\ \text{R}^4 \end{array} \text{N} - \text{R}^3
 \end{array}$$

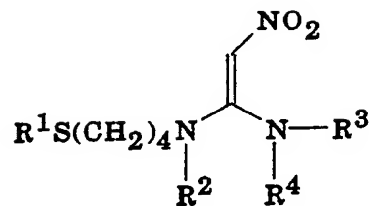
| | R ¹ | R ² | R ³ | R ⁴ | | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|----------------------------------|----------------|----------------|--|----------------|----------------------------------|----------------|----------------|
| 10 | Me | H | Me | H | | Me | Et | Et | H |
| | Me | Me | Me | H | | Me | n-Pr | Et | H |
| | Me | Et | Me | H | | Me | CHO | Et | H |
| | Me | n-Pr | Me | H | | Me | CH ₂ CN | Et | H |
| 15 | Me | CHO | Me | H | | Me | COCH ₃ | Et | H |
| | Me | CH ₂ CN | Me | H | | Me | CH ₂ NMe ₂ | Et | H |
| | Me | COCH ₃ | Me | H | | Et | H | Me | H |
| | Me | CH ₂ NMe ₂ | Me | H | | Et | Me | Me | H |
| | Me | H | Me | Me | | Et | CHO | Me | H |
| 20 | Me | Me | Me | Me | | Et | CH ₂ CN | Me | H |
| | Me | Et | Me | Me | | Et | H | Me | Me |
| | Me | n-Pr | Me | Me | | Et | Me | Me | Me |
| | Me | CHO | Me | Me | | Et | CHO | Me | Me |
| | Me | CH ₂ CN | Me | Me | | Et | CH ₂ CN | Me | Me |
| 25 | Me | COCH ₃ | Me | Me | | Et | H | Et | H |
| | Me | CH ₂ NMe ₂ | Me | Me | | Et | Me | Et | H |
| | Me | H | Et | H | | Et | CHO | Et | H |
| | Me | Me | Et | H | | Et | CH ₂ CN | Et | H |

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TABLE 9

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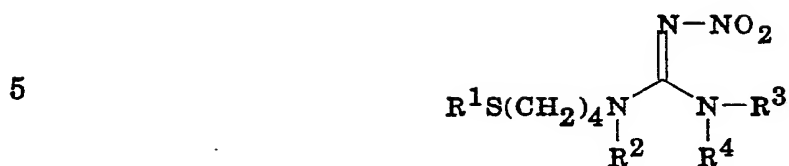


| 10 | R ¹ | R ² | R ³ | R ⁴ | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|----------------------------------|----------------|----------------|----------------|----------------------------------|----------------|----------------|
| | Me | H | Me | H | Me | Et | Et | H |
| | Me | Me | Me | H | Me | n-Pr | Et | H |
| | Me | Et | Me | H | Me | CHO | Et | H |
| | Me | n-Pr | Me | H | Me | CH ₂ CN | Et | H |
| 15 | Me | CHO | Me | H | Me | COCH ₃ | Et | H |
| | Me | CH ₂ CN | Me | H | Me | CH ₂ NMe ₂ | Et | H |
| | Me | COCH ₃ | Me | H | Et | H | Me | H |
| | Me | CH ₂ NMe ₂ | Me | H | Et | Me | Me | H |
| 20 | Me | H | Me | Me | Et | CHO | Me | H |
| | Me | Me | Me | Me | Et | CH ₂ CN | Me | H |
| | Me | Et | Me | Me | Et | H | Me | Me |
| | Me | n-Pr | Me | Me | Et | Me | Me | Me |
| | Me | CHO | Me | Me | Et | CHO | Me | Me |
| | Me | CH ₂ CN | Me | Me | Et | CH ₂ CN | Me | Me |
| 25 | Me | COCH ₃ | Me | Me | Et | H | Et | H |
| | Me | CH ₂ NMe ₂ | Me | Me | Et | Me | Et | H |
| | Me | H | Et | H | Et | CHO | Et | H |
| | Me | Me | Et | H | Et | CH ₂ CN | Et | H |

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TABLE 10



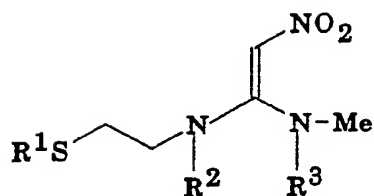
| | R ¹ | R ² | R ³ | R ⁴ | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|----------------------------------|----------------|----------------|----------------|----------------------------------|----------------|----------------|
| 10 | Me | H | Me | H | Me | Et | Et | H |
| | Me | Me | Me | H | Me | n-Pr | Et | H |
| | Me | Et | Me | H | Me | CHO | Et | H |
| | Me | n-Pr | Me | H | Me | CH ₂ CN | Et | H |
| 15 | Me | CHO | Me | H | Me | COCH ₃ | Et | H |
| | Me | CH ₂ CN | Me | H | Me | CH ₂ NMe ₂ | Et | H |
| | Me | COCH ₃ | Me | H | Et | H | Me | H |
| | Me | CH ₂ NMe ₂ | Me | H | Et | Me | Me | H |
| | Me | H | Me | Me | Et | CHO | Me | H |
| 20 | Me | Me | Me | Me | Et | CH ₂ CN | Me | H |
| | Me | Et | Me | Me | Et | H | Me | Me |
| | Me | n-Pr | Me | Me | Et | Me | Me | Me |
| | Me | CHO | Me | Me | Et | CHO | Me | Me |
| | Me | CH ₂ CN | Me | Me | Et | CH ₂ CN | Me | Me |
| 25 | Me | COCH ₃ | Me | Me | Et | H | Et | H |
| | Me | CH ₂ NMe ₂ | Me | Me | Et | Me | Et | H |
| | Me | H | Et | H | Et | CHO | Et | H |
| | Me | Me | Et | H | Et | CH ₂ CN | Et | H |

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TABLE 11

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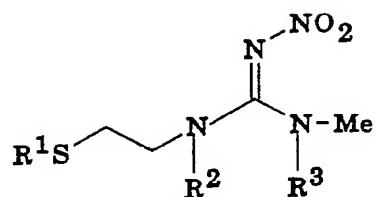
| | R ¹ | R ² | R ³ | | R ¹ | R ² | R ³ |
|----|----------------|---|----------------|--|----------------|----------------------------------|---|
| 10 | Me | n-Pr | H | | Me | OCH ₃ | allyl |
| | Me | n-Bu | H | | Me | SO ₂ CH ₃ | allyl |
| | Me | i-Pr | H | | Me | CH ₂ CN | allyl |
| | Me | s-Bu | H | | Me | N(CH ₃) ₂ | allyl |
| 15 | Me | i-Bu | H | | Me | CH ₂ Ph | allyl |
| | Me | t-Bu | H | | Me | CHO | propargyl |
| | Me | CHO | H | | Me | OCH ₃ | propargyl |
| | Me | COCH ₃ | H | | Me | SO ₂ CH ₃ | propargyl |
| | Me | OCH ₃ | H | | Me | CH ₂ CN | propargyl |
| 20 | Me | CH ₂ O(CH ₂) ₂ OCH ₃ | H | | Me | N(CH ₃) ₂ | propargyl |
| | Me | SO ₂ CH ₃ | H | | Me | CH ₂ Ph | propargyl |
| | Me | CH ₂ CN | H | | Me | CHO | CHO |
| | Me | N(CH ₃) ₂ | H | | Me | COCH ₃ | CHO |
| | Me | CH ₂ Ph | H | | Me | OCH ₃ | CHO |
| 25 | Me | n-Pr | Me | | Me | N(CH ₃) ₂ | CHO |
| | Me | n-Bu | Me | | Me | CH ₂ CN | CHO |
| | Me | CHO | Me | | Me | OCH ₃ | COCH ₃ |
| | Me | OCH ₃ | Me | | Me | CH ₂ CN | COCH ₃ |
| | Me | SO ₂ CH ₃ | Me | | Me | CHO | CH ₂ O(CH ₂) ₂ OCH ₃ |
| 30 | Me | CH ₂ CN | Me | | Me | OCH ₃ | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | N(CH ₃) ₂ | Me | | Me | CHO | SO ₂ CH ₃ |
| | Me | CH ₂ Ph | Me | | Me | OCH ₃ | SO ₂ CH ₃ |
| | Me | CHO | allyl | | Me | CH ₂ CN | SO ₂ CH ₃ |

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| | R ¹ | R ² | R ³ | | R ¹ | R ² | R ³ |
|----|----------------|----------------------------------|--------------------|--|------------------------------------|----------------|----------------|
| 5 | Me | CHO | CH ₂ CN | | n-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ CN | | n-Bu | CHO | H |
| | Me | CH ₂ CN | CH ₂ CN | | (CH ₂) ₂ Cl | CHO | H |
| | Me | N(CH ₃) ₂ | CH ₂ CN | | c-Pr | CHO | H |
| | Me | n-Pr | CH ₂ Ph | | c-pentyl | CHO | H |
| 10 | Me | CHO | CH ₂ Ph | | CH ₂ -c-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ Ph | | | | |
| | Me | CH ₂ CN | CH ₂ Ph | | | | |
| | Me | CH ₂ Ph | CH ₂ Ph | | | | |
| | Et | n-Pr | H | | | | |
| 15 | Et | CHO | H | | | | |
| | Et | OCH ₃ | H | | | | |
| | Et | SO ₂ CH ₃ | H | | | | |
| | Et | CH ₂ CN | H | | | | |
| | Et | n-Pr | Me | | | | |
| 20 | Et | CHO | Me | | | | |
| | Et | OCH ₃ | Me | | | | |
| | Et | SO ₂ CH ₃ | Me | | | | |
| | Et | CH ₂ CN | Me | | | | |
| | Et | CHO | CHO | | | | |
| 25 | Et | COCH ₃ | CHO | | | | |
| | Et | OCH ₃ | CHO | | | | |
| | Et | CH ₂ CN | CHO | | | | |
| | Et | CHO | COCH ₃ | | | | |
| | Et | COCH ₃ | COCH ₃ | | | | |
| 30 | Et | OCH ₃ | COCH ₃ | | | | |
| | Et | CH ₂ CN | COCH ₃ | | | | |

TABLE 12

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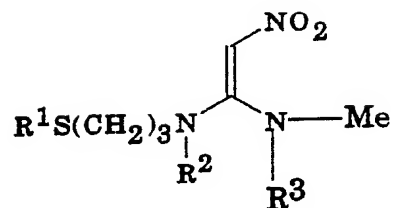
| | R ¹ | R ² | R ³ | | R ¹ | R ² | R ³ |
|----|----------------|---|----------------|--|----------------|----------------------------------|---|
| 10 | Me | n-Pr | H | | Me | OCH ₃ | allyl |
| | Me | n-Bu | H | | Me | SO ₂ CH ₃ | allyl |
| | Me | i-Pr | H | | Me | CH ₂ CN | allyl |
| | Me | s-Bu | H | | Me | N(CH ₃) ₂ | allyl |
| 15 | Me | i-Bu | H | | Me | CH ₂ Ph | allyl |
| | Me | t-Bu | H | | Me | CHO | propargyl |
| | Me | CHO | H | | Me | OCH ₃ | propargyl |
| | Me | COCH ₃ | H | | Me | SO ₂ CH ₃ | propargyl |
| | Me | OCH ₃ | H | | Me | CH ₂ CN | propargyl |
| 20 | Me | CH ₂ O(CH ₂) ₂ OCH ₃ | H | | Me | N(CH ₃) ₂ | propargyl |
| | Me | SO ₂ CH ₃ | H | | Me | CH ₂ Ph | propargyl |
| | Me | CH ₂ CN | H | | Me | CHO | CHO |
| | Me | N(CH ₃) ₂ | H | | Me | COCH ₃ | CHO |
| | Me | CH ₂ Ph | H | | Me | OCH ₃ | CHO |
| 25 | Me | n-Pr | Me | | Me | N(CH ₃) ₂ | CHO |
| | Me | n-Bu | Me | | Me | CH ₂ CN | CHO |
| | Me | CHO | Me | | Me | OCH ₃ | COCH ₃ |
| | Me | OCH ₃ | Me | | Me | CH ₂ CN | COCH ₃ |
| | Me | SO ₂ CH ₃ | Me | | Me | CHO | CH ₂ O(CH ₂) ₂ OCH ₃ |
| 30 | Me | CH ₂ CN | Me | | Me | OCH ₃ | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | N(CH ₃) ₂ | Me | | Me | CHO | SO ₂ CH ₃ |
| | Me | CH ₂ Ph | Me | | Me | OCH ₃ | SO ₂ CH ₃ |
| | Me | CHO | allyl | | Me | CH ₂ CN | SO ₂ CH ₃ |

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| | R ¹ | R ² | R ³ | | R ¹ | R ² | R ³ |
|----|----------------|----------------------------------|--------------------|--|------------------------------------|----------------|----------------|
| 5 | Me | CHO | CH ₂ CN | | n-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ CN | | n-Bu | CHO | H |
| | Me | CH ₂ CN | CH ₂ CN | | (CH ₂) ₂ Cl | CHO | H |
| | Me | N(CH ₃) ₂ | CH ₂ CN | | c-Pr | CHO | H |
| | Me | n-Pr | CH ₂ Ph | | c-pentyl | CHO | H |
| 10 | Me | CHO | CH ₂ Ph | | CH ₂ -c-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ Ph | | | | |
| | Me | CH ₂ CN | CH ₂ Ph | | | | |
| | Me | CH ₂ Ph | CH ₂ Ph | | | | |
| | Et | n-Pr | H | | | | |
| 15 | Et | CHO | H | | | | |
| | Et | OCH ₃ | H | | | | |
| | Et | SO ₂ CH ₃ | H | | | | |
| | Et | CH ₂ CN | H | | | | |
| | Et | n-Pr | Me | | | | |
| 20 | Et | CHO | Me | | | | |
| | Et | OCH ₃ | Me | | | | |
| | Et | SO ₂ CH ₃ | Me | | | | |
| | Et | CH ₂ CN | Me | | | | |
| | Et | CHO | CHO | | | | |
| 25 | Et | COCH ₃ | CHO | | | | |
| | Et | OCH ₃ | CHO | | | | |
| | Et | CH ₂ CN | CHO | | | | |
| | Et | CHO | COCH ₃ | | | | |
| | Et | COCH ₃ | COCH ₃ | | | | |
| 30 | Et | OCH ₃ | COCH ₃ | | | | |
| | Et | CH ₂ CN | COCH ₃ | | | | |

TABLE 13

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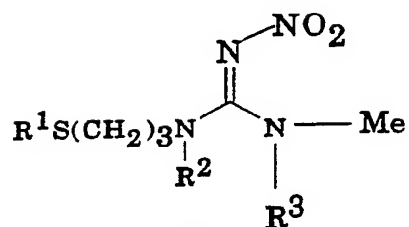
| | R ¹ | R ² | R ³ | R ¹ | R ² | R ³ |
|----|----------------|---|----------------|----------------|----------------------------------|---|
| 10 | Me | n-Pr | H | Me | OCH ₃ | allyl |
| | Me | n-Bu | H | Me | SO ₂ CH ₃ | allyl |
| | Me | i-Pr | H | Me | CH ₂ CN | allyl |
| 15 | Me | s-Bu | H | Me | N(CH ₃) ₂ | allyl |
| | Me | i-Bu | H | Me | CH ₂ Ph | allyl |
| | Me | t-Bu | H | Me | CHO | propargyl |
| | Me | CHO | H | Me | OCH ₃ | propargyl |
| | Me | COCH ₃ | H | Me | SO ₂ CH ₃ | propargyl |
| 20 | Me | OCH ₃ | H | Me | CH ₂ CN | propargyl |
| | Me | CH ₂ O(CH ₂) ₂ OCH ₃ | H | Me | N(CH ₃) ₂ | propargyl |
| | Me | SO ₂ CH ₃ | H | Me | CH ₂ Ph | propargyl |
| | Me | CH ₂ CN | H | Me | CHO | CHO |
| | Me | N(CH ₃) ₂ | H | Me | COCH ₃ | CHO |
| 25 | Me | CH ₂ Ph | H | Me | OCH ₃ | CHO |
| | Me | n-Pr | Me | Me | N(CH ₃) ₂ | CHO |
| | Me | n-Bu | Me | Me | CH ₂ CN | CHO |
| | Me | CHO | Me | Me | OCH ₃ | COCH ₃ |
| | Me | OCH ₃ | Me | Me | CH ₂ CN | COCH ₃ |
| 30 | Me | SO ₂ CH ₃ | Me | Me | CHO | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | CH ₂ CN | Me | Me | OCH ₃ | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | N(CH ₃) ₂ | Me | Me | CHO | SO ₂ CH ₃ |
| | Me | CH ₂ Ph | Me | Me | OCH ₃ | SO ₂ CH ₃ |
| | Me | CHO | allyl | Me | CH ₂ CN | SO ₂ CH ₃ |
| 35 | | | | | | |

| | R ¹ | R ² | R ³ | R ¹ | R ² | R ³ |
|----|----------------|----------------------------------|--------------------|------------------------------------|----------------|----------------|
| 5 | Me | CHO | CH ₂ CN | n-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ CN | n-Bu | CHO | H |
| | Me | CH ₂ CN | CH ₂ CN | (CH ₂) ₂ Cl | CHO | H |
| | Me | N(CH ₃) ₂ | CH ₂ CN | c-Pr | CHO | H |
| | Me | n-Pr | CH ₂ Ph | c-pentyl | CHO | H |
| 10 | Me | CHO | CH ₂ Ph | CH ₂ -c-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ Ph | | | |
| | Me | CH ₂ CN | CH ₂ Ph | | | |
| | Me | CH ₂ Ph | CH ₂ Ph | | | |
| | Et | n-Pr | H | | | |
| 15 | Et | CHO | H | | | |
| | Et | OCH ₃ | H | | | |
| | Et | SO ₂ CH ₃ | H | | | |
| | Et | CH ₂ CN | H | | | |
| | Et | n-Pr | Me | | | |
| 20 | Et | CHO | Me | | | |
| | Et | OCH ₃ | Me | | | |
| | Et | SO ₂ CH ₃ | Me | | | |
| | Et | CH ₂ CN | Me | | | |
| | Et | CHO | CHO | | | |
| 25 | Et | COCH ₃ | CHO | | | |
| | Et | OCH ₃ | CHO | | | |
| | Et | CH ₂ CN | CHO | | | |
| | Et | CHO | COCH ₃ | | | |
| | Et | COCH ₃ | COCH ₃ | | | |
| 30 | Et | OCH ₃ | COCH ₃ | | | |
| | Et | CH ₂ CN | COCH ₃ | | | |

35

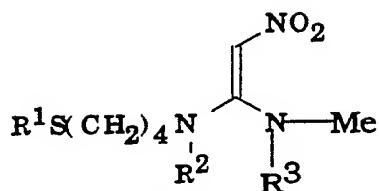
TABLE 14

5



| 10 | R ¹ | R ² | R ³ | R ¹ | R ² | R ³ |
|----|----------------|---|----------------|----------------|----------------------------------|---|
| | Me | n-Pr | H | Me | OCH ₃ | allyl |
| | Me | n-Bu | H | Me | SO ₂ CH ₃ | allyl |
| | Me | i-Pr | H | Me | CH ₂ CN | allyl |
| 15 | Me | s-Bu | H | Me | N(CH ₃) ₂ | allyl |
| | Me | i-Bu | H | Me | CH ₂ Ph | allyl |
| | Me | t-Bu | H | Me | CHO | propargyl |
| | Me | CHO | H | Me | OCH ₃ | propargyl |
| | Me | COCH ₃ | H | Me | SO ₂ CH ₃ | propargyl |
| 20 | Me | OCH ₃ | H | Me | CH ₂ CN | propargyl |
| | Me | CH ₂ O(CH ₂) ₂ OCH ₃ | H | Me | N(CH ₃) ₂ | propargyl |
| | Me | SO ₂ CH ₃ | H | Me | CH ₂ Ph | propargyl |
| | Me | CH ₂ CN | H | Me | CHO | CHO |
| | Me | N(CH ₃) ₂ | H | Me | COCH ₃ | CHO |
| 25 | Me | CH ₂ Ph | H | Me | OCH ₃ | CHO |
| | Me | n-Pr | Me | Me | N(CH ₃) ₂ | CHO |
| | Me | n-Bu | Me | Me | CH ₂ CN | CHO |
| | Me | CHO | Me | Me | OCH ₃ | COCH ₃ |
| | Me | OCH ₃ | Me | Me | CH ₂ CN | COCH ₃ |
| 30 | Me | SO ₂ CH ₃ | Me | Me | CHO | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | CH ₂ CN | Me | Me | OCH ₃ | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | N(CH ₃) ₂ | Me | Me | CHO | SO ₂ CH ₃ |
| | Me | CH ₂ Ph | Me | Me | OCH ₃ | SO ₂ CH ₃ |
| | Me | CHO | allyl | Me | CH ₂ CN | SO ₂ CH ₃ |
| 35 | | | | | | |

| | R ¹ | R ² | R ³ | | R ¹ | R ² | R ³ |
|----|----------------|----------------------------------|--------------------|--|------------------------------------|----------------|----------------|
| 5 | Me | CHO | CH ₂ CN | | n-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ CN | | n-Bu | CHO | H |
| | Me | CH ₂ CN | CH ₂ CN | | (CH ₂) ₂ Cl | CHO | H |
| | Me | N(CH ₃) ₂ | CH ₂ CN | | c-Pr | CHO | H |
| | Me | n-Pr | CH ₂ Ph | | c-pentyl | CHO | H |
| 10 | Me | CHO | CH ₂ Ph | | CH ₂ -c-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ Ph | | | | |
| | Me | CH ₂ CN | CH ₂ Ph | | | | |
| | Me | CH ₂ Ph | CH ₂ Ph | | | | |
| | Et | n-Pr | H | | | | |
| 15 | Et | CHO | H | | | | |
| | Et | OCH ₃ | H | | | | |
| | Et | SO ₂ CH ₃ | H | | | | |
| | Et | CH ₂ CN | H | | | | |
| | Et | n-Pr | Me | | | | |
| 20 | Et | CHO | Me | | | | |
| | Et | OCH ₃ | Me | | | | |
| | Et | SO ₂ CH ₃ | Me | | | | |
| | Et | CH ₂ CN | Me | | | | |
| | Et | CHO | CHO | | | | |
| 25 | Et | COCH ₃ | CHO | | | | |
| | Et | OCH ₃ | CHO | | | | |
| | Et | CH ₂ CN | CHO | | | | |
| | Et | CHO | COCH ₃ | | | | |
| | Et | COCH ₃ | COCH ₃ | | | | |
| 30 | Et | OCH ₃ | COCH ₃ | | | | |
| | Et | CH ₂ CN | COCH ₃ | | | | |

TABLE 15

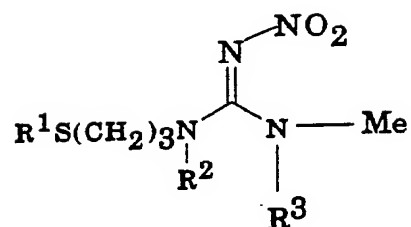
| | R ¹ | R ² | R ³ | | R ¹ | R ² | R ³ |
|----|----------------|---|----------------|--|----------------|----------------------------------|---|
| 10 | Me | n-Pr | H | | Me | OCH ₃ | allyl |
| | Me | n-Bu | H | | Me | SO ₂ CH ₃ | allyl |
| | Me | i-Pr | H | | Me | CH ₂ CN | allyl |
| | Me | s-Bu | H | | Me | N(CH ₃) ₂ | allyl |
| 15 | Me | i-Bu | H | | Me | CH ₂ Ph | allyl |
| | Me | t-Bu | H | | Me | CHO | propargyl |
| | Me | CHO | H | | Me | OCH ₃ | propargyl |
| | Me | COCH ₃ | H | | Me | SO ₂ CH ₃ | propargyl |
| | Me | OCH ₃ | H | | Me | CH ₂ CN | propargyl |
| 20 | Me | CH ₂ O(CH ₂) ₂ OCH ₃ | H | | Me | N(CH ₃) ₂ | propargyl |
| | Me | SO ₂ CH ₃ | H | | Me | CH ₂ Ph | propargyl |
| | Me | CH ₂ CN | H | | Me | CHO | CHO |
| | Me | N(CH ₃) ₂ | H | | Me | COCH ₃ | CHO |
| | Me | CH ₂ Ph | H | | Me | OCH ₃ | CHO |
| 25 | Me | n-Pr | Me | | Me | N(CH ₃) ₂ | CHO |
| | Me | n-Bu | Me | | Me | CH ₂ CN | CHO |
| | Me | CHO | Me | | Me | OCH ₃ | COCH ₃ |
| | Me | OCH ₃ | Me | | Me | CH ₂ CN | COCH ₃ |
| | Me | SO ₂ CH ₃ | Me | | Me | CHO | CH ₂ O(CH ₂) ₂ OCH ₃ |
| 30 | Me | CH ₂ CN | Me | | Me | OCH ₃ | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | N(CH ₃) ₂ | Me | | Me | CHO | SO ₂ CH ₃ |
| | Me | CH ₂ Ph | Me | | Me | OCH ₃ | SO ₂ CH ₃ |
| | Me | CHO | allyl | | Me | CH ₂ CN | SO ₂ CH ₃ |

35

| | R ¹ | R ² | R ³ | | R ¹ | R ² | R ³ |
|----|----------------|----------------------------------|--------------------|--|------------------------------------|----------------|----------------|
| 5 | Me | CHO | CH ₂ CN | | n-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ CN | | n-Bu | CHO | H |
| | Me | CH ₂ CN | CH ₂ CN | | (CH ₂) ₂ Cl | CHO | H |
| | Me | N(CH ₃) ₂ | CH ₂ CN | | c-Pr | CHO | H |
| | Me | n-Pr | CH ₂ Ph | | c-pentyl | CHO | H |
| 10 | Me | CHO | CH ₂ Ph | | CH ₂ -c-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ Ph | | | | |
| | Me | CH ₂ CN | CH ₂ Ph | | | | |
| | Me | CH ₂ Ph | CH ₂ Ph | | | | |
| | Et | n-Pr | H | | | | |
| 15 | Et | CHO | H | | | | |
| | Et | OCH ₃ | H | | | | |
| | Et | SO ₂ CH ₃ | H | | | | |
| | Et | CH ₂ CN | H | | | | |
| | Et | n-Pr | Me | | | | |
| 20 | Et | CHO | Me | | | | |
| | Et | OCH ₃ | Me | | | | |
| | Et | SO ₂ CH ₃ | Me | | | | |
| | Et | CH ₂ CN | Me | | | | |
| | Et | CHO | CHO | | | | |
| 25 | Et | COCH ₃ | CHO | | | | |
| | Et | OCH ₃ | CHO | | | | |
| | Et | CH ₂ CN | CHO | | | | |
| | Et | CHO | COCH ₃ | | | | |
| | Et | COCH ₃ | COCH ₃ | | | | |
| 30 | Et | OCH ₃ | COCH ₃ | | | | |
| | Et | CH ₂ CN | COCH ₃ | | | | |

TABLE 16

5

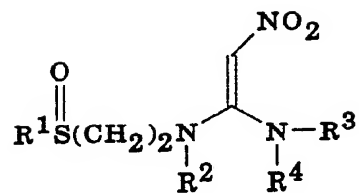


| 10 | R ¹ | R ² | R ³ | R ¹ | R ² | R ³ |
|----|----------------|---|----------------|----------------|----------------------------------|---|
| | Me | n-Pr | H | Me | OCH ₃ | allyl |
| | Me | n-Bu | H | Me | SO ₂ CH ₃ | allyl |
| | Me | i-Pr | H | Me | CH ₂ CN | allyl |
| 15 | Me | s-Bu | H | Me | N(CH ₃) ₂ | allyl |
| | Me | i-Bu | H | Me | CH ₂ Ph | allyl |
| | Me | t-Bu | H | Me | CHO | propargyl |
| | Me | CHO | H | Me | OCH ₃ | propargyl |
| | Me | COCH ₃ | H | Me | SO ₂ CH ₃ | propargyl |
| 20 | Me | OCH ₃ | H | Me | CH ₂ CN | propargyl |
| | Me | CH ₂ O(CH ₂) ₂ OCH ₃ | H | Me | N(CH ₃) ₂ | propargyl |
| | Me | SO ₂ CH ₃ | H | Me | CH ₂ Ph | propargyl |
| | Me | CH ₂ CN | H | Me | CHO | CHO |
| | Me | N(CH ₃) ₂ | H | Me | COCH ₃ | CHO |
| 25 | Me | CH ₂ Ph | H | Me | OCH ₃ | CHO |
| | Me | n-Pr | Me | Me | N(CH ₃) ₂ | CHO |
| | Me | n-Bu | Me | Me | CH ₂ CN | CHO |
| | Me | CHO | Me | Me | OCH ₃ | COCH ₃ |
| | Me | OCH ₃ | Me | Me | CH ₂ CN | COCH ₃ |
| 30 | Me | SO ₂ CH ₃ | Me | Me | CHO | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | CH ₂ CN | Me | Me | OCH ₃ | CH ₂ O(CH ₂) ₂ OCH ₃ |
| | Me | N(CH ₃) ₂ | Me | Me | CHO | SO ₂ CH ₃ |
| | Me | CH ₂ Ph | Me | Me | OCH ₃ | SO ₂ CH ₃ |
| | Me | CHO | allyl | Me | CH ₂ CN | SO ₂ CH ₃ |
| 35 | | | | | | |

| | R ¹ | R ² | R ³ | R ¹ | R ² | R ³ |
|----|----------------|----------------------------------|--------------------|------------------------------------|----------------|----------------|
| 5 | Me | CHO | CH ₂ CN | n-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ CN | n-Bu | CHO | H |
| | Me | CH ₂ CN | CH ₂ CN | (CH ₂) ₂ Cl | CHO | H |
| | Me | N(CH ₃) ₂ | CH ₂ CN | c-Pr | CHO | H |
| | Me | n-Pr | CH ₂ Ph | c-pentyl | CHO | H |
| 10 | Me | CHO | CH ₂ Ph | CH ₂ -c-Pr | CHO | H |
| | Me | OCH ₃ | CH ₂ Ph | | | |
| | Me | CH ₂ CN | CH ₂ Ph | | | |
| | Me | CH ₂ Ph | CH ₂ Ph | | | |
| 15 | Et | n-Pr | H | | | |
| | Et | CHO | H | | | |
| | Et | OCH ₃ | H | | | |
| | Et | SO ₂ CH ₃ | H | | | |
| | Et | CH ₂ CN | H | | | |
| 20 | Et | n-Pr | Me | | | |
| | Et | CHO | Me | | | |
| | Et | OCH ₃ | Me | | | |
| | Et | SO ₂ CH ₃ | Me | | | |
| | Et | CH ₂ CN | Me | | | |
| 25 | Et | CHO | CHO | | | |
| | Et | COCH ₃ | CHO | | | |
| | Et | OCH ₃ | CHO | | | |
| | Et | CH ₂ CN | CHO | | | |
| | Et | CHO | COCH ₃ | | | |
| | Et | COCH ₃ | COCH ₃ | | | |
| 30 | Et | OCH ₃ | COCH ₃ | | | |
| | Et | CH ₂ CN | COCH ₃ | | | |

TABLE 17

5

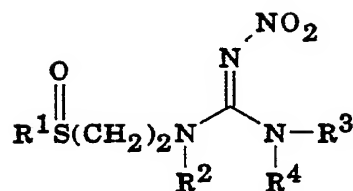


| | R ¹ | R ² | R ³ | R ⁴ | | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|---------------------------------|----------------|----------------|--|----------------|----------------------------------|----------------|----------------|
| 10 | Me | H | H | H | | Me | N(CH ₃) ₂ | H | H |
| | Me | Me | H | H | | Me | N(CH ₃) ₂ | Me | H |
| | Me | H | Me | H | | Me | N(CH ₃) ₂ | CHO | H |
| | Me | H | Me | Me | | Me | N(CH ₃) ₂ | CHO | Me |
| 15 | Me | H | Et | H | | Me | N(CH ₃) ₂ | Et | H |
| | Me | Me | Me | H | | Et | H | Me | H |
| | Me | Me | Me | Me | | Et | H | Me | Me |
| | Me | Me | Et | H | | Et | H | Et | H |
| | Me | Me | c-Pr | H | | Et | H | CHO | H |
| 20 | Me | Me | n-Pr | H | | Et | H | CHO | Me |
| | Me | Me | Me | CHO | | Et | Me | Me | H |
| | Me | CHO | H | H | | Et | Me | CHO | H |
| | Me | CHO | Me | H | | Et | Me | CHO | Me |
| | Me | SO ₂ CH ₃ | Me | H | | Et | CHO | Me | H |
| 25 | Me | SO ₂ CH ₃ | H | H | | Et | CHO | Et | H |
| | Me | OCH ₃ | H | H | | Et | CHO | Me | Me |
| | Me | OCH ₃ | Me | H | | | | | |
| | Me | OCH ₃ | Me | CHO | | | | | |
| | Me | CH ₂ CN | Me | H | | | | | |
| 30 | Me | CH ₂ CN | Me | Me | | | | | |
| | Me | CH ₂ CN | Et | H | | | | | |

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TABLE 18

5

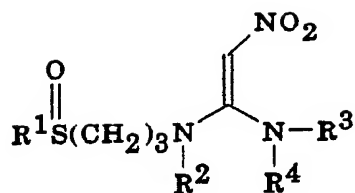


| | R ¹ | R ² | R ³ | R ⁴ | | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|---------------------------------|----------------|----------------|--|----------------|----------------------------------|----------------|----------------|
| 10 | Me | H | H | H | | Me | N(CH ₃) ₂ | H | H |
| | Me | Me | H | H | | Me | N(CH ₃) ₂ | Me | H |
| | Me | H | Me | H | | Me | N(CH ₃) ₂ | CHO | H |
| | Me | H | Me | Me | | Me | N(CH ₃) ₂ | CHO | Me |
| 15 | Me | H | Et | H | | Me | N(CH ₃) ₂ | Et | H |
| | Me | Me | Me | H | | Et | H | Me | H |
| | Me | Me | Me | Me | | Et | H | Me | Me |
| | Me | Me | Et | H | | Et | H | Et | H |
| | Me | Me | c-Pr | H | | Et | H | CHO | H |
| 20 | Me | Me | n-Pr | H | | Et | H | CHO | Me |
| | Me | Me | Me | CHO | | Et | Me | Me | H |
| | Me | CHO | H | H | | Et | Me | CHO | H |
| | Me | CHO | Me | H | | Et | Me | CHO | Me |
| | Me | SO ₂ CH ₃ | Me | H | | Et | CHO | Me | H |
| 25 | Me | SO ₂ CH ₃ | H | H | | Et | CHO | Et | H |
| | Me | OCH ₃ | H | H | | Et | CHO | Me | Me |
| | Me | OCH ₃ | Me | H | | | | | |
| | Me | OCH ₃ | Me | CHO | | | | | |
| | Me | CH ₂ CN | Me | H | | | | | |
| 30 | Me | CH ₂ CN | Me | Me | | | | | |
| | Me | CH ₂ CN | Et | H | | | | | |

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TABLE 19

5

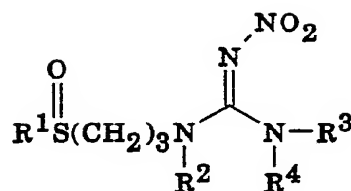


| | R ¹ | R ² | R ³ | R ⁴ | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|---------------------------------|----------------|----------------|----------------|----------------------------------|----------------|----------------|
| 10 | Me | H | H | H | Me | N(CH ₃) ₂ | H | H |
| | Me | Me | H | H | Me | N(CH ₃) ₂ | Me | H |
| | Me | H | Me | H | Me | N(CH ₃) ₂ | CHO | H |
| | Me | H | Me | Me | Me | N(CH ₃) ₂ | CHO | Me |
| 15 | Me | H | Et | H | Me | N(CH ₃) ₂ | Et | H |
| | Me | Me | Me | H | Et | H | Me | H |
| | Me | Me | Me | Me | Et | H | Me | Me |
| | Me | Me | Et | H | Et | H | Et | H |
| | Me | Me | c-Pr | H | Et | H | CHO | H |
| 20 | Me | Me | n-Pr | H | Et | H | CHO | Me |
| | Me | Me | Me | CHO | Et | Me | Me | H |
| | Me | CHO | H | H | Et | Me | CHO | H |
| | Me | CHO | Me | H | Et | Me | CHO | Me |
| | Me | SO ₂ CH ₃ | Me | H | Et | CHO | Me | H |
| 25 | Me | SO ₂ CH ₃ | H | H | Et | CHO | Et | H |
| | Me | OCH ₃ | H | H | Et | CHO | Me | Me |
| | Me | OCH ₃ | Me | H | | | | |
| | Me | OCH ₃ | Me | CHO | | | | |
| | Me | CH ₂ CN | Me | H | | | | |
| 30 | Me | CH ₂ CN | Me | Me | | | | |
| | Me | CH ₂ CN | Et | H | | | | |

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TABLE 20

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| | R ¹ | R ² | R ³ | R ⁴ | | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|---------------------------------|----------------|----------------|--|----------------|----------------------------------|----------------|----------------|
| 10 | Me | H | H | H | | Me | N(CH ₃) ₂ | H | H |
| | Me | Me | H | H | | Me | N(CH ₃) ₂ | Me | H |
| | Me | H | Me | H | | Me | N(CH ₃) ₂ | CHO | H |
| | Me | H | Me | Me | | Me | N(CH ₃) ₂ | CHO | Me |
| 15 | Me | H | Et | H | | Me | N(CH ₃) ₂ | Et | H |
| | Me | Me | Me | H | | Et | H | Me | H |
| | Me | Me | Me | Me | | Et | H | Me | Me |
| | Me | Me | Et | H | | Et | H | Et | H |
| | Me | Me | c-Pr | H | | Et | H | CHO | H |
| 20 | Me | Me | n-Pr | H | | Et | H | CHO | Me |
| | Me | Me | Me | CHO | | Et | Me | Me | H |
| | Me | CHO | H | H | | Et | Me | CHO | H |
| | Me | CHO | Me | H | | Et | Me | CHO | Me |
| | Me | SO ₂ CH ₃ | Me | H | | Et | CHO | Me | H |
| 25 | Me | SO ₂ CH ₃ | H | H | | Et | CHO | Et | H |
| | Me | OCH ₃ | H | H | | Et | CHO | Me | Me |
| | Me | OCH ₃ | Me | H | | | | | |
| | Me | OCH ₃ | Me | CHO | | | | | |
| | Me | CH ₂ CN | Me | H | | | | | |
| 30 | Me | CH ₂ CN | Me | Me | | | | | |
| | Me | CH ₂ CN | Et | H | | | | | |

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TABLE 21

5

$$\begin{array}{c}
 \text{NO}_2 \\
 \diagup \\
 \text{R}^1\text{S}(=\text{O})_2(\text{CH}_2)_2\text{N}(\text{R}^2)\text{C}=\text{N}(\text{R}^3)\text{R}^4
 \end{array}$$

| | | | | | | | | |
|----|----------------|---------------------------------|----------------|----------------|----------------|----------------------------------|----------------|----------------|
| 10 | R ¹ | R ² | R ³ | R ⁴ | R ¹ | R ² | R ³ | R ⁴ |
| | Me | H | H | H | Me | N(CH ₃) ₂ | H | H |
| | Me | Me | H | H | Me | N(CH ₃) ₂ | Me | H |
| | Me | H | Me | H | Me | N(CH ₃) ₂ | CHO | H |
| 15 | Me | H | Me | Me | Me | N(CH ₃) ₂ | CHO | Me |
| | Me | H | Et | H | Me | N(CH ₃) ₂ | Et | H |
| | Me | Me | Me | H | Et | H | Me | H |
| | Me | Me | Me | Me | Et | H | Me | Me |
| | Me | Me | Et | H | Et | H | Et | H |
| 20 | Me | Me | c-Pr | H | Et | H | CHO | H |
| | Me | Me | n-Pr | H | Et | H | CHO | Me |
| | Me | Me | Me | CHO | Et | Me | Me | H |
| | Me | CHO | H | H | Et | Me | CHO | H |
| | Me | CHO | Me | H | Et | Me | CHO | Me |
| 25 | Me | SO ₂ CH ₃ | Me | H | Et | CHO | Me | H |
| | Me | SO ₂ CH ₃ | H | H | Et | CHO | Et | H |
| | Me | OCH ₃ | H | H | Et | CHO | Me | Me |
| | Me | OCH ₃ | Me | H | | | | |
| | Me | OCH ₃ | Me | CHO | | | | |
| 30 | Me | CH ₂ CN | Me | H | | | | |
| | Me | CH ₂ CN | Me | Me | | | | |
| | Me | CH ₂ CN | Et | H | | | | |

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TABLE 22

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$$\begin{array}{c}
 \text{O} \\
 \parallel \\
 \text{R}^1\text{S}(\text{CH}_2)_2\text{N} \begin{array}{c} \diagup \text{N} \text{NO}_2 \\ \diagdown \end{array} \\
 \parallel \\
 \text{O}
 \end{array}
 \begin{array}{c}
 \text{R}^2 \\
 | \\
 \text{N} \\
 | \\
 \text{R}^4
 \end{array}
 \begin{array}{c}
 \text{R}^3 \\
 | \\
 \text{N} \\
 | \\
 \text{R}^4
 \end{array}$$

| 10 | R ¹ | R ² | R ³ | R ⁴ | R ¹ | R ² | R ³ | R ⁴ |
|----|----------------|---------------------------------|----------------|----------------|----------------|----------------------------------|----------------|----------------|
| | Me | H | H | H | Me | N(CH ₃) ₂ | H | H |
| | Me | Me | H | H | Me | N(CH ₃) ₂ | Me | H |
| | Me | H | Me | H | Me | N(CH ₃) ₂ | CHO | H |
| 15 | Me | H | Me | Me | Me | N(CH ₃) ₂ | CHO | Me |
| | Me | H | Et | H | Me | N(CH ₃) ₂ | Et | H |
| | Me | Me | Me | H | Et | H | Me | H |
| | Me | Me | Me | Me | Et | H | Me | Me |
| | Me | Me | Et | H | Et | H | Et | H |
| 20 | Me | Me | c-Pr | H | Et | H | CHO | H |
| | Me | Me | n-Pr | H | Et | H | CHO | Me |
| | Me | Me | Me | CHO | Et | Me | Me | H |
| | Me | CHO | H | H | Et | Me | CHO | H |
| | Me | CHO | Me | H | Et | Me | CHO | Me |
| 25 | Me | SO ₂ CH ₃ | Me | H | Et | CHO | Me | H |
| | Me | SO ₂ CH ₃ | H | H | Et | CHO | Et | H |
| | Me | OCH ₃ | H | H | Et | CHO | Me | Me |
| | Me | OCH ₃ | Me | H | | | | |
| | Me | OCH ₃ | Me | CHO | | | | |
| 30 | Me | CH ₂ CN | Me | H | | | | |
| | Me | CH ₂ CN | Me | Me | | | | |
| | Me | CH ₂ CN | Et | H | | | | |

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TABLE 23

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$$\begin{array}{c}
 \text{NO}_2 \\
 \diagup \\
 \text{R}^1\text{S}(=\text{O})_2(\text{CH}_2)_3\text{N}(\text{R}^2)=\text{C}(\text{N}(\text{R}^3)\text{R}^4)
 \end{array}$$

| | | | | | | | | |
|----|----------------|---------------------------------|----------------|----------------|----------------|----------------------------------|----------------|----------------|
| 10 | R ¹ | R ² | R ³ | R ⁴ | R ¹ | R ² | R ³ | R ⁴ |
| | Me | H | H | H | Me | N(CH ₃) ₂ | H | H |
| | Me | Me | H | H | Me | N(CH ₃) ₂ | Me | H |
| | Me | H | Me | H | Me | N(CH ₃) ₂ | CHO | H |
| 15 | Me | H | Me | Me | Me | N(CH ₃) ₂ | CHO | Me |
| | Me | H | Et | H | Me | N(CH ₃) ₂ | Et | H |
| | Me | Me | Me | H | Et | H | Me | H |
| | Me | Me | Me | Me | Et | H | Me | Me |
| | Me | Me | Et | H | Et | H | Et | H |
| 20 | Me | Me | c-Pr | H | Et | H | CHO | H |
| | Me | Me | n-Pr | H | Et | H | CHO | Me |
| | Me | Me | Me | CHO | Et | Me | Me | H |
| | Me | CHO | H | H | Et | Me | CHO | H |
| | Me | CHO | Me | H | Et | Me | CHO | Me |
| 25 | Me | SO ₂ CH ₃ | Me | H | Et | CHO | Me | H |
| | Me | SO ₂ CH ₃ | H | H | Et | CHO | Et | H |
| | Me | OCH ₃ | H | H | Et | CHO | Me | Me |
| | Me | OCH ₃ | Me | H | | | | |
| | Me | OCH ₃ | Me | CHO | | | | |
| 30 | Me | CH ₂ CN | Me | H | | | | |
| | Me | CH ₂ CN | Me | Me | | | | |
| | Me | CH ₂ CN | Et | H | | | | |

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TABLE 24

5

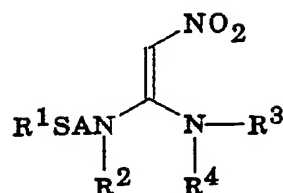
$$\begin{array}{c}
 \text{O} \\
 \parallel \\
 \text{R}^1\text{S}(\text{CH}_2)_3\text{N} \begin{array}{c} \diagup \text{N} \text{---} \text{NO}_2 \\ \diagdown \end{array} \\
 \parallel \\
 \text{O}
 \end{array}
 \begin{array}{c}
 \text{R}^2 \\
 \text{N} \\
 \text{R}^4
 \end{array}
 \begin{array}{c}
 \text{R}^3
 \end{array}$$

| | | | | | | | | |
|----|----------------|---------------------------------|----------------|----------------|----------------|----------------------------------|----------------|----------------|
| 10 | R ¹ | R ² | R ³ | R ⁴ | R ¹ | R ² | R ³ | R ⁴ |
| | Me | H | H | H | Me | N(CH ₃) ₂ | H | H |
| | Me | Me | H | H | Me | N(CH ₃) ₂ | Me | H |
| | Me | H | Me | H | Me | N(CH ₃) ₂ | CHO | H |
| 15 | Me | H | Me | Me | Me | N(CH ₃) ₂ | CHO | Me |
| | Me | H | Et | H | Me | N(CH ₃) ₂ | Et | H |
| | Me | Me | Me | H | Et | H | Me | H |
| | Me | Me | Me | Me | Et | H | Me | Me |
| | Me | Me | Et | H | Et | H | Et | H |
| 20 | Me | Me | c-Pr | H | Et | H | CHO | H |
| | Me | Me | n-Pr | H | Et | H | CHO | Me |
| | Me | Me | Me | CHO | Et | Me | Me | H |
| | Me | CHO | H | H | Et | Me | CHO | H |
| | Me | CHO | Me | H | Et | Me | CHO | Me |
| 25 | Me | SO ₂ CH ₃ | Me | H | Et | CHO | Me | H |
| | Me | SO ₂ CH ₃ | H | H | Et | CHO | Et | H |
| | Me | OCH ₃ | H | H | Et | CHO | Me | Me |
| | Me | OCH ₃ | Me | H | | | | |
| | Me | OCH ₃ | Me | CHO | | | | |
| 30 | Me | CH ₂ CN | Me | H | | | | |
| | Me | CH ₂ CN | Me | Me | | | | |
| | Me | CH ₂ CN | Et | H | | | | |

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TABLE 25

5

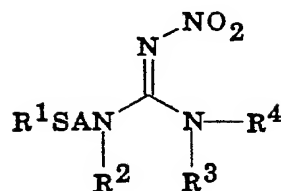


| | A | R ¹ | R ² | R ³ | R ⁴ | A | R ¹ | R ² | R ³ | R ⁴ |
|----|---|----------------|----------------|----------------|----------------|---|----------------|----------------|----------------|----------------|
| 10 | CH ₂ CH(CH ₃) | Me | H | Me | H | CH(CH ₃)(CH ₂) ₃ | Me | Me | Me | H |
| | CH(CH ₃)CH ₂ | Me | H | Me | H | CH ₂ CH(n-Pr) | Me | Me | Me | H |
| | (CH ₂) ₂ CH(CH ₃) | Me | H | Me | H | CH(n-Pr)CH ₂ | Me | Me | Me | H |
| | CH(CH ₃)CH ₂ CH ₂ | Me | H | Me | H | CH ₂ CH(Me) | Me | H | Me | Me |
| 15 | CH ₂ CH(CH ₃)CH ₂ | Me | H | Me | H | CH(Me)CH ₂ | Me | H | Me | Me |
| | CH(CH ₃)(CH ₂) ₃ | Me | H | Me | H | (CH ₂) ₂ CH(Me) | Me | H | Me | Me |
| | (CH ₂) ₃ CH(CH ₃) | Me | H | Me | H | CH(Me)(CH ₂) ₂ | Me | H | Me | Me |
| | CH ₂ CH(CH ₃)(CH ₂) ₂ | Me | H | Me | H | CH ₂ CH(Et) | Me | H | Me | Me |
| | (CH ₂) ₂ CH(CH ₃)CH ₂ | Me | H | Me | H | CH(Et)CH ₂ | Me | H | Me | Me |
| 20 | CH ₂ CH(Et) | Me | H | Me | H | (CH ₂) ₃ CH(Me) | Me | H | Me | Me |
| | CH(Et)CH ₂ | Me | H | Me | H | CH(Me)(CH ₂) ₃ | Me | H | Me | Me |
| | CH ₂ CH(Et)CH ₂ | Me | H | Me | H | CH ₂ CH(n-Pr) | Me | H | Me | Me |
| | CH ₂ CH(n-Pr) | Me | H | Me | H | CH(n-Pr)CH ₂ | Me | H | Me | Me |
| | CH(n-Pr)CH ₂ | Me | H | Me | H | CH ₂ CH(CH ₃) | Me | H | Et | H |
| 25 | CH ₂ CH(n-Pr)CH ₂ | Me | H | Me | H | CH ₂ CH(CH ₃) | Me | H | n-Pr | H |
| | CH ₂ CH(CH ₃) | Me | Me | Me | H | CH ₂ CH(CH ₃) | Me | H | n-Bu | H |
| | CH(CH ₃)CH ₂ | Me | Me | Me | H | CH ₂ CH(CH ₃) | Me | CHO | Me | H |
| | (CH ₂) ₂ CH(CH ₃) | Me | Me | Me | H | CH ₂ CH(CH ₃) | Me | CHO | Et | H |
| | CH(CH ₃)(CH ₂) ₂ | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | H | Et | H |
| 30 | CH ₂ CH(CH ₃)CH ₂ | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | H | n-Pr | H |
| | CH ₂ CH(Et) | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | H | n-Bu | H |
| | CH(Et)CH ₂ | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | CHO | Me | H |
| | (CH ₂) ₃ CH(CH ₃) | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | CHO | Et | H |

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TABLE 26

5

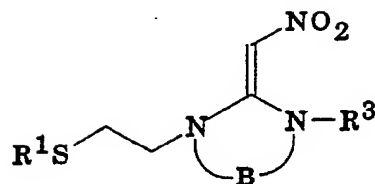


| | A | R ¹ | R ² | R ³ | R ⁴ | A | R ¹ | R ² | R ³ | R ⁴ |
|----|---|----------------|----------------|----------------|----------------|---|----------------|----------------|----------------|----------------|
| 10 | CH ₂ CH(CH ₃) | Me | H | Me | H | CH(CH ₃)(CH ₂) ₃ | Me | Me | Me | H |
| | CH(CH ₃)CH ₂ | Me | H | Me | H | CH ₂ CH(n-Pr) | Me | Me | Me | H |
| | (CH ₂) ₂ CH(CH ₃) | Me | H | Me | H | CH(n-Pr)CH ₂ | Me | Me | Me | H |
| | CH(CH ₃)CH ₂ CH ₂ | Me | H | Me | H | CH ₂ CH(Me) | Me | H | Me | Me |
| 15 | CH ₂ CH(CH ₃)CH ₂ | Me | H | Me | H | CH(Me)CH ₂ | Me | H | Me | Me |
| | CH(CH ₃)(CH ₂) ₃ | Me | H | Me | H | (CH ₂) ₂ CH(Me) | Me | H | Me | Me |
| | (CH ₂) ₃ CH(CH ₃) | Me | H | Me | H | CH(Me)(CH ₂) ₂ | Me | H | Me | Me |
| | CH ₂ CH(CH ₃)(CH ₂) ₂ | Me | H | Me | H | CH ₂ CH(Et) | Me | H | Me | Me |
| | (CH ₂) ₂ CH(CH ₃)CH ₂ | Me | H | Me | H | CH(Et)CH ₂ | Me | H | Me | Me |
| 20 | CH ₂ CH(Et) | Me | H | Me | H | (CH ₂) ₃ CH(Me) | Me | H | Me | Me |
| | CH(Et)CH ₂ | Me | H | Me | H | CH(Me)(CH ₂) ₃ | Me | H | Me | Me |
| | CH ₂ CH(Et)CH ₂ | Me | H | Me | H | CH ₂ CH(n-Pr) | Me | H | Me | Me |
| | CH ₂ CH(n-Pr) | Me | H | Me | H | CH(n-Pr)CH ₂ | Me | H | Me | Me |
| | CH(n-Pr)CH ₂ | Me | H | Me | H | CH ₂ CH(CH ₃) | Me | H | Et | H |
| 25 | CH ₂ CH(n-Pr)CH ₂ | Me | H | Me | H | CH ₂ CH(CH ₃) | Me | H | n-Pr | H |
| | CH ₂ CH(CH ₃) | Me | Me | Me | H | CH ₂ CH(CH ₃) | Me | H | n-Bu | H |
| | CH(CH ₃)CH ₂ | Me | Me | Me | H | CH ₂ CH(CH ₃) | Me | CHO | Me | H |
| | (CH ₂) ₂ CH(CH ₃) | Me | Me | Me | H | CH ₂ CH(CH ₃) | Me | CHO | Et | H |
| | CH(CH ₃)(CH ₂) ₂ | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | H | Et | H |
| 30 | CH ₂ CH(CH ₃)CH ₂ | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | H | n-Pr | H |
| | CH ₂ CH(Et) | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | H | n-Bu | H |
| | CH(Et)CH ₂ | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | CHO | Me | H |
| | (CH ₂) ₃ CH(CH ₃) | Me | Me | Me | H | CH(CH ₃)CH ₂ | Me | CHO | Et | H |

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TABLE 27

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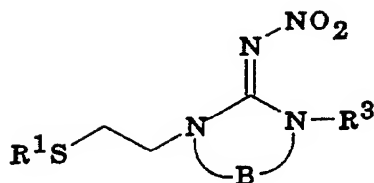
| | R ¹ | B | R ³ | | R ¹ | B | R ³ |
|----|----------------|---------------------------------|----------------------------------|--|----------------|---------------------------------|----------------------------------|
| 10 | Me | CH ₂ CH ₂ | H | | Me | (CH ₂) ₃ | CHO |
| | Me | CH ₂ CH ₂ | Me | | Me | (CH ₂) ₃ | COMe |
| | Me | CH ₂ CH ₂ | Et | | Me | (CH ₂) ₃ | CH ₂ CN |
| | Me | CH ₂ CH ₂ | n-Pr | | Me | (CH ₂) ₃ | CH ₂ NMe ₂ |
| 15 | Me | CH ₂ CH ₂ | CHO | | Me | (CH ₂) ₃ | OMe |
| | Me | CH ₂ CH ₂ | COMe | | Me | (CH ₂) ₃ | allyl |
| | Me | CH ₂ CH ₂ | CH ₂ CN | | Me | (CH ₂) ₃ | CH ₂ CCH |
| | Me | CH ₂ CH ₂ | CH ₂ NMe ₂ | | Me | CH ₂ CH ₂ | CH ₂ CCH |
| | Me | CH ₂ CH ₂ | OMe | | Et | (CH ₂) ₃ | H |
| 20 | Me | CH ₂ CH ₂ | SO ₂ Me | | Et | (CH ₂) ₃ | Me |
| | Me | CH ₂ CH ₂ | allyl | | Et | (CH ₂) ₃ | Et |
| | Et | CH ₂ CH ₂ | H | | Et | (CH ₂) ₃ | CHO |
| | Et | CH ₂ CH ₂ | Me | | Et | (CH ₂) ₃ | CH ₂ CN |
| | Et | CH ₂ CH ₂ | Et | | Et | (CH ₂) ₃ | CH ₂ NMe ₂ |
| 25 | Et | CH ₂ CH ₂ | CHO | | n-Pr | CH ₂ CH ₂ | H |
| | Et | CH ₂ CH ₂ | CH ₂ CN | | n-Pr | CH ₂ CH ₂ | Me |
| | Et | CH ₂ CH ₂ | CH ₂ NMe ₂ | | n-Pr | CH ₂ CH ₂ | CHO |
| | Me | (CH ₂) ₃ | H | | n-Pr | CH ₂ CH ₂ | CH ₂ CN |
| | Me | (CH ₂) ₃ | Me | | n-Pr | CH ₂ CH ₂ | CH ₂ NMe ₂ |
| 30 | Me | (CH ₂) ₃ | Et | | c-Pr | CH ₂ CH ₂ | H |
| | Me | (CH ₂) ₃ | n-Pr | | c-Pr | CH ₂ CH ₂ | CH ₂ CN |

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| | R ¹ | B | R ³ | | R ¹ | B | R ³ |
|----|-----------------------|---------------------------------|----------------------------------|--|-----------------------|------|----------------------------------|
| 5 | CH ₂ -c-Pr | CH ₂ CH ₂ | CH ₂ CN | | Et | CHCH | CH ₂ CN |
| | CH ₂ -c-Pr | CH ₂ CH ₂ | H | | Et | CHCH | CH ₂ NMe ₂ |
| | n-Pr | (CH ₂) ₃ | H | | n-Pr | CHCH | H |
| | n-Pr | (CH ₂) ₃ | Me | | n-Pr | CHCH | Me |
| | n-Pr | (CH ₂) ₃ | CHO | | n-Pr | CHCH | CHO |
| 10 | n-Pr | (CH ₂) ₃ | CH ₂ CN | | n-Pr | CHCH | CH ₂ CN |
| | n-Pr | (CH ₂) ₃ | CH ₂ NMe ₂ | | n-Pr | CHCH | CH ₂ NMe ₂ |
| | c-Pr | (CH ₂) ₃ | H | | c-Pr | CHCH | H |
| | c-Pr | (CH ₂) ₃ | CH ₂ CN | | c-Pr | CHCH | CH ₂ CN |
| | CH ₂ -c-Pr | (CH ₂) ₃ | H | | CH ₂ -c-Pr | CHCH | H |
| 15 | CH ₂ -c-Pr | (CH ₂) ₃ | CH ₂ CN | | CH ₂ -c-Pr | CHCH | CH ₂ CN |
| | Me | CHCH | H | | | | |
| | Me | CHCH | Me | | | | |
| | Me | CHCH | Et | | | | |
| | Me | CHCH | n-Pr | | | | |
| 20 | Me | CHCH | CHO | | | | |
| | Me | CHCH | COMe | | | | |
| | Me | CHCH | CH ₂ CN | | | | |
| | Me | CHCH | CH ₂ NMe ₂ | | | | |
| | Me | CHCH | OMe | | | | |
| 25 | Me | CHCH | SO ₂ Me | | | | |
| | Me | CHCH | allyl | | | | |
| | Me | CHCH | CH ₂ CCH | | | | |
| | Et | CHCH | H | | | | |
| | Et | CHCH | Me | | | | |
| 30 | Et | CHCH | Et | | | | |
| | Et | CHCH | CHO | | | | |

TABLE 28

5



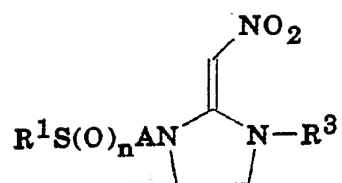
| | R ¹ | B | R ³ | | R ¹ | B | R ³ |
|----|----------------|---------------------------------|----------------------------------|--|----------------|---------------------------------|----------------------------------|
| 10 | Me | CH ₂ CH ₂ | H | | Me | (CH ₂) ₃ | CHO |
| | Me | CH ₂ CH ₂ | Me | | Me | (CH ₂) ₃ | COMe |
| | Me | CH ₂ CH ₂ | Et | | Me | (CH ₂) ₃ | CH ₂ CN |
| | Me | CH ₂ CH ₂ | n-Pr | | Me | (CH ₂) ₃ | CH ₂ NMe ₂ |
| 15 | Me | CH ₂ CH ₂ | CHO | | Me | (CH ₂) ₃ | OMe |
| | Me | CH ₂ CH ₂ | COMe | | Me | (CH ₂) ₃ | allyl |
| | Me | CH ₂ CH ₂ | CH ₂ CN | | Me | (CH ₂) ₃ | CH ₂ CCH |
| | Me | CH ₂ CH ₂ | CH ₂ NMe ₂ | | Me | CH ₂ CH ₂ | CH ₂ CCH |
| | Me | CH ₂ CH ₂ | OMe | | Et | (CH ₂) ₃ | H |
| 20 | Me | CH ₂ CH ₂ | SO ₂ Me | | Et | (CH ₂) ₃ | Me |
| | Me | CH ₂ CH ₂ | allyl | | Et | (CH ₂) ₃ | Et |
| | Et | CH ₂ CH ₂ | H | | Et | (CH ₂) ₃ | CHO |
| | Et | CH ₂ CH ₂ | Me | | Et | (CH ₂) ₃ | CH ₂ CN |
| | Et | CH ₂ CH ₂ | Et | | Et | (CH ₂) ₃ | CH ₂ NMe ₂ |
| 25 | Et | CH ₂ CH ₂ | CHO | | n-Pr | CH ₂ CH ₂ | H |
| | Et | CH ₂ CH ₂ | CH ₂ CN | | n-Pr | CH ₂ CH ₂ | Me |
| | Et | CH ₂ CH ₂ | CH ₂ NMe ₂ | | n-Pr | CH ₂ CH ₂ | CHO |
| | Me | (CH ₂) ₃ | H | | n-Pr | CH ₂ CH ₂ | CH ₂ CN |
| | Me | (CH ₂) ₃ | Me | | n-Pr | CH ₂ CH ₂ | CH ₂ NMe ₂ |
| 30 | Me | (CH ₂) ₃ | Et | | c-Pr | CH ₂ CH ₂ | H |
| | Me | (CH ₂) ₃ | n-Pr | | c-Pr | CH ₂ CH ₂ | CH ₂ CN |

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| | R ¹ | R | R ³ | | R ¹ | R | R ³ |
|----|-----------------------|---------------------------------|----------------------------------|--|-----------------------|------|----------------------------------|
| 5 | CH ₂ -c-Pr | CH ₂ CH ₂ | CH ₂ CN | | Et | CHCH | CH ₂ CN |
| | CH ₂ -c-Pr | CH ₂ CH ₂ | H | | Et | CHCH | CH ₂ NMe ₂ |
| | n-Pr | (CH ₂) ₃ | H | | n-Pr | CHCH | H |
| | n-Pr | (CH ₂) ₃ | Me | | n-Pr | CHCH | Me |
| | n-Pr | (CH ₂) ₃ | CHO | | n-Pr | CHCH | CHO |
| 10 | n-Pr | (CH ₂) ₃ | CH ₂ CN | | n-Pr | CHCH | CH ₂ CN |
| | n-Pr | (CH ₂) ₃ | CH ₂ NMe ₂ | | n-Pr | CHCH | CH ₂ NMe ₂ |
| | c-Pr | (CH ₂) ₃ | H | | c-Pr | CHCH | H |
| | c-Pr | (CH ₂) ₃ | CH ₂ CN | | c-Pr | CHCH | CH ₂ CN |
| | CH ₂ -c-Pr | (CH ₂) ₃ | H | | CH ₂ -c-Pr | CHCH | H |
| 15 | CH ₂ -c-Pr | (CH ₂) ₃ | CH ₂ CN | | CH ₂ -c-Pr | CHCH | CH ₂ CN |
| | Me | CHCH | H | | | | |
| | Me | CHCH | Me | | | | |
| | Me | CHCH | Et | | | | |
| | Me | CHCH | n-Pr | | | | |
| 20 | Me | CHCH | CHO | | | | |
| | Me | CHCH | COMe | | | | |
| | Me | CHCH | CH ₂ CN | | | | |
| | Me | CHCH | CH ₂ NMe ₂ | | | | |
| | Me | CHCH | OMe | | | | |
| 25 | Me | CHCH | SO ₂ Me | | | | |
| | Me | CHCH | allyl | | | | |
| | Me | CHCH | CH ₂ CCH | | | | |
| | Et | CHCH | H | | | | |
| | Et | CHCH | Me | | | | |
| 30 | Et | CHCH | Et | | | | |
| | Et | CHCH | CHO | | | | |

TABLE 29

5

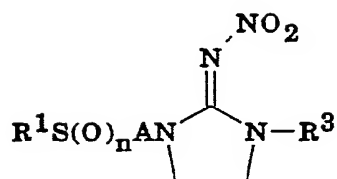


| | R^1 | n | A | R^3 |
|----|--------------|-----|--------------------------|------------------------|
| 10 | Me | 0 | $(\text{CH}_2)_3$ | H |
| | Me | 0 | $(\text{CH}_2)_3$ | Me |
| | Me | 0 | $(\text{CH}_2)_3$ | CHO |
| | Me | 0 | $(\text{CH}_2)_3$ | CH_2CN |
| 15 | Me | 1 | CH_2CH_2 | H |
| | Me | 1 | CH_2CH_2 | Me |
| | Me | 1 | CH_2CH_2 | CHO |
| | Me | 1 | CH_2CH_2 | CH_2CN |
| | Me | 1 | $(\text{CH}_2)_3$ | H |
| 20 | Me | 1 | $(\text{CH}_2)_3$ | Me |
| | Me | 1 | $(\text{CH}_2)_3$ | CHO |
| | Me | 1 | $(\text{CH}_2)_3$ | CH_2CN |
| | Me | 2 | CH_2CH_2 | H |
| | Me | 2 | CH_2CH_2 | Me |
| 25 | Me | 2 | CH_2CH_2 | CHO |
| | Me | 2 | CH_2CH_2 | CH_2CN |
| | Me | 2 | $(\text{CH}_2)_3$ | H |
| | Me | 2 | $(\text{CH}_2)_3$ | Me |
| | Me | 2 | $(\text{CH}_2)_3$ | CHO |
| 30 | Me | 2 | $(\text{CH}_2)_3$ | CH_2CN |

35

TABLE 30

5

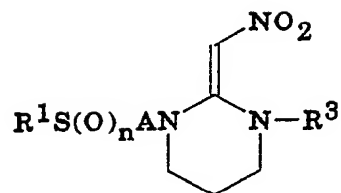


| 10 | R^1 | n | Δ | R^3 |
|----|--------------|-----|--------------------------|------------------------|
| | Me | 0 | $(\text{CH}_2)_3$ | H |
| | Me | 0 | $(\text{CH}_2)_3$ | Me |
| | Me | 0 | $(\text{CH}_2)_3$ | CHO |
| | Me | 0 | $(\text{CH}_2)_3$ | CH_2CN |
| 15 | Me | 1 | CH_2CH_2 | H |
| | Me | 1 | CH_2CH_2 | Me |
| | Me | 1 | CH_2CH_2 | CHO |
| | Me | 1 | CH_2CH_2 | CH_2CN |
| | Me | 1 | $(\text{CH}_2)_3$ | H |
| 20 | Me | 1 | $(\text{CH}_2)_3$ | Me |
| | Me | 1 | $(\text{CH}_2)_3$ | CHO |
| | Me | 1 | $(\text{CH}_2)_3$ | CH_2CN |
| | Me | 2 | CH_2CH_2 | H |
| | Me | 2 | CH_2CH_2 | Me |
| 25 | Me | 2 | CH_2CH_2 | CHO |
| | Me | 2 | CH_2CH_2 | CH_2CN |
| | Me | 2 | $(\text{CH}_2)_3$ | H |
| | Me | 2 | $(\text{CH}_2)_3$ | Me |
| | Me | 2 | $(\text{CH}_2)_3$ | CHO |
| 30 | Me | 2 | $(\text{CH}_2)_3$ | CH_2CN |

35

TABLE 31

5

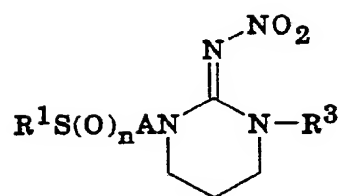


| 10 | R ¹ | n | A | R ³ |
|----|----------------|---|---------------------------------|--------------------|
| | Me | 0 | (CH ₂) ₃ | H |
| | Me | 0 | (CH ₂) ₃ | Me |
| | Me | 0 | (CH ₂) ₃ | CHO |
| | Me | 0 | (CH ₂) ₃ | CH ₂ CN |
| 15 | Me | 1 | CH ₂ CH ₂ | H |
| | Me | 1 | CH ₂ CH ₂ | Me |
| | Me | 1 | CH ₂ CH ₂ | CHO |
| | Me | 1 | CH ₂ CH ₂ | CH ₂ CN |
| | Me | 1 | (CH ₂) ₃ | H |
| 20 | Me | 1 | (CH ₂) ₃ | Me |
| | Me | 1 | (CH ₂) ₃ | CHO |
| | Me | 1 | (CH ₂) ₃ | CH ₂ CN |
| | Me | 2 | CH ₂ CH ₂ | H |
| | Me | 2 | CH ₂ CH ₂ | Me |
| 25 | Me | 2 | CH ₂ CH ₂ | CHO |
| | Me | 2 | CH ₂ CH ₂ | CH ₂ CN |
| | Me | 2 | (CH ₂) ₃ | H |
| | Me | 2 | (CH ₂) ₃ | Me |
| | Me | 2 | (CH ₂) ₃ | CHO |
| 30 | Me | 2 | (CH ₂) ₃ | CH ₂ CN |

35

TABLE 32

5

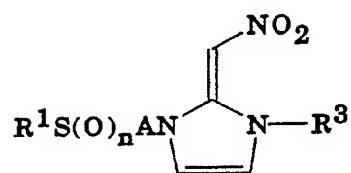


| 10 | R^1 | n | A | R^3 |
|----|--------------|-----|--------------------------|------------------------|
| | Me | 0 | $(\text{CH}_2)_3$ | H |
| | Me | 0 | $(\text{CH}_2)_3$ | Me |
| | Me | 0 | $(\text{CH}_2)_3$ | CHO |
| | Me | 0 | $(\text{CH}_2)_3$ | CH_2CN |
| 15 | Me | 1 | CH_2CH_2 | H |
| | Me | 1 | CH_2CH_2 | Me |
| | Me | 1 | CH_2CH_2 | CHO |
| | Me | 1 | CH_2CH_2 | CH_2CN |
| 20 | Me | 1 | $(\text{CH}_2)_3$ | H |
| | Me | 1 | $(\text{CH}_2)_3$ | Me |
| | Me | 1 | $(\text{CH}_2)_3$ | CHO |
| | Me | 1 | $(\text{CH}_2)_3$ | CH_2CN |
| | Me | 2 | CH_2CH_2 | H |
| | Me | 2 | CH_2CH_2 | Me |
| 25 | Me | 2 | CH_2CH_2 | CHO |
| | Me | 2 | CH_2CH_2 | CH_2CN |
| | Me | 2 | $(\text{CH}_2)_3$ | H |
| | Me | 2 | $(\text{CH}_2)_3$ | Me |
| 30 | Me | 2 | $(\text{CH}_2)_3$ | CHO |
| | Me | 2 | $(\text{CH}_2)_3$ | CH_2CN |

35

TABLE 33

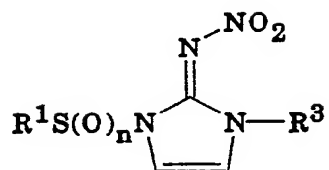
5



| | R^1 | n | A | R^3 |
|----|--------------|-----|--------------------------|------------------------|
| 10 | Me | 0 | $(\text{CH}_2)_3$ | H |
| | Me | 0 | $(\text{CH}_2)_3$ | Me |
| | Me | 0 | $(\text{CH}_2)_3$ | CHO |
| | Me | 0 | $(\text{CH}_2)_3$ | CH_2CN |
| 15 | Me | 1 | CH_2CH_2 | H |
| | Me | 1 | CH_2CH_2 | Me |
| | Me | 1 | CH_2CH_2 | CHO |
| | Me | 1 | CH_2CH_2 | CH_2CN |
| | Me | 1 | $(\text{CH}_2)_3$ | H |
| 20 | Me | 1 | $(\text{CH}_2)_3$ | Me |
| | Me | 1 | $(\text{CH}_2)_3$ | CHO |
| | Me | 1 | $(\text{CH}_2)_3$ | CH_2CN |
| | Me | 2 | CH_2CH_2 | H |
| | Me | 2 | CH_2CH_2 | Me |
| 25 | Me | 2 | CH_2CH_2 | CHO |
| | Me | 2 | CH_2CH_2 | CH_2CN |
| | Me | 2 | $(\text{CH}_2)_3$ | H |
| | Me | 2 | $(\text{CH}_2)_3$ | Me |
| | Me | 2 | $(\text{CH}_2)_3$ | CHO |
| 30 | Me | 2 | $(\text{CH}_2)_3$ | CH_2CN |

35

TABLE 34

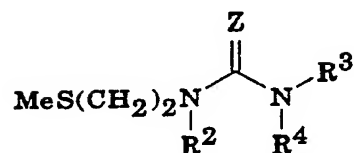


| | R ¹ | n | A | R ³ |
|----|----------------|---|---------------------------------|--------------------|
| 10 | Me | 0 | (CH ₂) ₃ | H |
| | Me | 0 | (CH ₂) ₃ | Me |
| | Me | 0 | (CH ₂) ₃ | CHO |
| | Me | 0 | (CH ₂) ₃ | CH ₂ CN |
| 15 | Me | 1 | CH ₂ CH ₂ | H |
| | Me | 1 | CH ₂ CH ₂ | Me |
| | Me | 1 | CH ₂ CH ₂ | CHO |
| | Me | 1 | CH ₂ CH ₂ | CH ₂ CN |
| | Me | 1 | (CH ₂) ₃ | H |
| 20 | Me | 1 | (CH ₂) ₃ | Me |
| | Me | 1 | (CH ₂) ₃ | CHO |
| | Me | 1 | (CH ₂) ₃ | CH ₂ CN |
| | Me | 2 | CH ₂ CH ₂ | H |
| | Me | 2 | CH ₂ CH ₂ | Me |
| 25 | Me | 2 | CH ₂ CH ₂ | CHO |
| | Me | 2 | CH ₂ CH ₂ | CH ₂ CN |
| | Me | 2 | (CH ₂) ₃ | H |
| | Me | 2 | (CH ₂) ₃ | Me |
| | Me | 2 | (CH ₂) ₃ | CHO |
| 30 | Me | 2 | (CH ₂) ₃ | CH ₂ CN |

35

INDEX TABLE 1

5



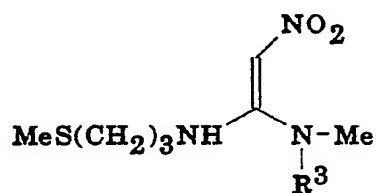
| | <u>COMPD</u> | <u>Z</u> | <u>R²</u> | <u>R³</u> | <u>R⁴</u> | <u>m.p.°C</u> |
|----|--------------|-------------------|----------------------|--|----------------------|------------------------|
| 10 | 1 | CHNO ₂ | H | Me | Me | oil |
| | 2 | CHNO ₂ | H | Me | H | 131.5-133 ^a |
| | 3 | CHNO ₂ | H | Et | H | 85-87 |
| | 4 | CHNO ₂ | Me | Me | H | oil |
| | 5 | CHNO ₂ | H | MeS(CH ₂) ₂ | H | 142-143 |
| 15 | 6 | CHNO ₂ | H | CH ₂ -c-Pr | H | 139-140 |
| | 7 | CHNO ₂ | H | n-Pr | H | 99-100 |
| | 8 | CHNO ₂ | H | H | H | 146-150 (dec) |
| | 9 | CHNO ₂ | H | OMe | H | oil |
| | 10 | CHNO ₂ | H | n-Bu | H | 110-112 |
| 20 | 11 | CHNO ₂ | H | Me ₂ N(CH ₂) ₂ | H | oil |

^aRecrystallization from ethanol provided material identical to the compound melting at 131.5-133°C by ¹H and ¹³C NMR but with a melting point of 115-116°C.

25

30

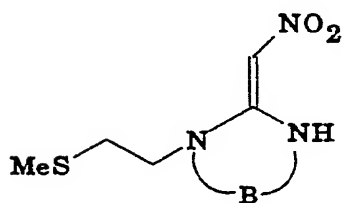
35

INDEX TABLE 2

10

| <u>CMPD</u> | <u>R³</u> | <u>m.p.°C</u> |
|-------------|----------------------|---------------|
| 12 | H | 75-77 |
| 13 | Me | oil |

15

INDEX TABLE 3

25

| <u>CMPD</u> | <u>B</u> | <u>m.p.°C</u> |
|-------------|---|---------------|
| 14 | CH ₂ CH ₂ | 102-104 |
| 15 | CH ₂ CH ₂ CH ₂ | 120-122 |

30

35

Formulation and Use

The compounds of this invention will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent or an organic solvent. Useful formulations of the compounds of Formula I can be prepared in conventional ways. They include dusts, granules, baits, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like. Many of these can be applied directly. Sprayable formulations can be extended in suitable media and used at spray volumes of from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations, broadly, contain from less than about 1% to 99% by weight of active ingredient(s) and at least one of a) about 0.1% to 20% surfactant(s) and b) about 5% to 99% solid or liquid diluent(s). More specifically, they will contain effective amounts of these ingredients in the following approximate proportions:

| <u>Percent by Weight</u> | | | |
|--------------------------|-------------------------|-------------------|----------------------|
| | <u>Active</u> | | |
| | <u>Ingredient</u> | <u>Diluent(s)</u> | <u>Surfactant(s)</u> |
| 20 | | | |
| | Wettable Powders | 25-90 | 0-74 |
| | Oil Suspensions, | 5-50 | 40-95 |
| 25 | Emulsions, Solutions, | | 0-15 |
| | (including Emulsifiable | | |
| | Concentrates) | | |
| | Dusts | 1-25 | 70-99 |
| | Granules, Baits | 0.01-95 | 5-99 |
| 30 | and Pellets | | 0-15 |
| | High Strength | 90-99 | 0-10 |
| | Compositions | | 0-2 |

Lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the

compound. Higher ratios of surfactant to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

5 Typical solid diluents are described in Watkins, et al., "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Dorland Books, Caldwell, New Jersey. The more absorptive diluents are preferred for wettable powders and the denser ones for dusts. Typical liquid diluents and solvents are described in Marsden, "Solvents Guide," 2nd Ed.,
10 Interscience, New York, 1950. Solubility under 0.1% is preferred for suspension concentrates; solution concentrates are preferably stable against phase separation at 0°C. "McCutcheon's Detergents and Emulsifiers Annual", Allured Publ. Corp., Ridgewood, New Jersey, as
15 Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc. Preferably, ingredients should be approved by the U.S. Environmental Protection Agency for the use
20 intended.

 The methods of making such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer or fluid energy mill. Suspensions are prepared by wet milling
25 (see, for example, U.S. 3,060,084). Granules and pellets can be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See J. E. Browning, "Agglomeration", Chemical Engineering, December 4, 1967, pages 147 and following, and
"Perry's Chemical Engineer's Handbook", 4th Ed., McGraw-Hill, New
30 York, 1963, pages 8 to 59 and following.

Example AEmulsifiable Concentrate

N-methyl-N'-[2-(methylthio)ethyl]-2-nitro-

- | | | |
|---|---------------------------------|-----|
| 5 | 1,1-ethenediamine | 20% |
| | blend of oil soluble sulfonates | |
| | and polyoxyethylene ethers | 10% |
| | isophorone | 70% |

- 10 The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in packaging operation to insure the absence of any extraneous undissolved material in the product.

Example BWettable Powder

N-methyl-N'-[2-(methylthio)ethyl]-2-nitro-

- | | | |
|----|-----------------------------------|-----|
| 15 | 1,1-ethenediamine | 30% |
| | sodium alkyl naphthalenesulfonate | 2% |
| | synthetic amorphous silica | 3% |
| 20 | kaolinite | 63% |

The active ingredient is mixed with the inert materials in a blender. After grinding in a hammermill, the material is re-blended and sifted through a 50 mesh screen.

Example CDust

- | | | |
|----|------------------------------|-----|
| 25 | Wettable powder of Example B | 10% |
| | pyrophyllite (powder) | 90% |
- 30 The wettable powder and the pyrophyllite diluent are thoroughly blended and then packaged. The product is suitable for use as a dust.

Example DGranule

N-methyl-N'-[2-(methylthio)ethyl]-2-nitro-

- | | | |
|----|-------------------|-----|
| 35 | 1,1-ethenediamine | 10% |
|----|-------------------|-----|

attapulgate granules (low volatile
matter, 0.71/0.30 mm; U.S.S. No.
25-50 sieves)

90%

- 5 The active ingredient is dissolved in a volatile solvent such as acetone and sprayed upon dedusted and pre-warmed attapulgate granules in a double cone blender. The acetone is then driven off by heating. The granules are then allowed to cool and are packaged.

10

Example EGranule

| | |
|-------------------------------|-----|
| Wett able powder of Example B | 15% |
| gypsum | 69% |
| potassium sulfate | 16% |

15

- The ingredients are blended in a rotating mixer and water sprayed on to accomplish granulation. When most of the material has reached the desired range of 0.1 to 0.42 mm (U.S.S. No. 18 to 40 sieves), the granules are removed, dried, and screened. Oversize material is crushed to produce additional material in the desired range. These granules contain
- 20 4.5% active ingredient.

Example FSolution

N-methyl-N'-[2-(methylthio)ethyl]-2-nitro-

- | | |
|------------------------|-----|
| 25 1,1-ethenediamine | 25% |
| N-methyl-pyrrolidone | 75% |

The ingredients are combined and stirred to produce a solution suitable for direct, low volume application.

30

Example GAqueous Suspension

N-methyl-N'-[2-(methylthio)ethyl]-2-nitro-

- | | |
|----------------------------|------|
| 1,1-ethenediamine | 2.0% |
| Isopropyl phosphoric ester | 0.2% |
| 35 White Carbon | 1.0% |

Finely powdered talc

96.8%

The ingredients are thoroughly blended and pulverized to make a driftless dust. The material can then be packaged.

5

Example H

Oil Suspension

N-methyl-N'-[2-(methylthio)ethyl]-2-nitro-
1,1-ethenediamine

35.0%

10 blend of polyalcohol carboxylic
 esters and oil soluble petroleum
 sulfonates

6.0%

 xylene range solvent

59.0%

15 The ingredients are combined and ground together in a sand mill
to produce particles substantially all below 5 microns. The product can
be used directly, extended with oils, or emulsified in water.

Example I

Bait Granules

20 N-methyl-N'-[2-(methylthio)ethyl]-2-nitro-
 1,1-ethenediamine

3.0%

 blend of polyethoxylated nonyl-
 phenols and sodium dodecyl-
 benzene sulfonates

9.0%

25 ground up corn cobs

88.0%

 The active ingredient and surfactant blend are dissolved in a
suitable solvent such as acetone and sprayed onto the ground corn cobs.
The granules are then dried and packaged.

30 Compounds of Formula I can also be mixed with one or more other
insecticides, fungicides, nematocides, bactericides, acaricides, or other
biologically active compounds to form a multi-component pesticide giving
an even broader spectrum of effective agricultural protection. Examples
of other agricultural protectants with which compounds of this invention
can be formulated are:

35

Insecticides:

- 3-hydroxy-N-methylcrotonamide(dimethylphosphate)ester
(monocrotophos)
- 5 methylcarbamic acid, ester with 2,3-dihydro-2,2-
dimethyl-7-benzofuranol (carbofuran)
- O-[2,4,5-trichloro-a-(chloromethyl)benzyl]phosphoric
acid, O',O'-dimethyl ester (tetrachlorvinphos)
- 2-mercaptosuccinic acid, diethyl ester, S-ester with
10 thionophosphoric acid, dimethyl ester (malathion)
- phosphorothioic acid, O,O-dimethyl, O-p-nitrophenyl
ester (methyl parathion)
- methylcarbamic acid, ester with a-naphthol (carbaryl)
- methyl O-(methylcarbamoyl)thiolacetohydroxamate
15 (methomyl)
- N'-(4-chloro-p-tolyl)-N,N-dimethylformamidine
(chlordimeform)
- O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidylphos-
phorothioate (diazinon)
- 20 octachlorocamphene (toxaphene)
- O-ethyl-O-p-nitrophenyl phenylphosphonothioate (EPN)
- (S)-a-cyano-m-phenoxybenzyl-(1R,3R)-3-(2,2-dibromo-
vinyl)-2,2-dimethylcyclopropanecarboxylate
(deltamethrin)
- 25 Methyl-N',N'-dimethyl-N-[(methylcarbamoyl)oxyl]-1-
thioox amimidate (oxamyl)
- cyano(3-phenoxyphenyl)-methyl-4-chloro-a-(1-methyl-
ethyl)benzeneacetate (fenvalerate)
- (3-phenoxyphenyl)methyl(+)-cis,trans-3-(2,2-dichloro
30 ethenyl)-2,2-dimethylcyclopropanecarboxylate (perme-
thrin)
- a-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-
dimethylcyclopropanecarboxylate (cypermethrin)
- O-ethyl-S-(p-chlorophenyl)ethylphosphonodithioate
35 (profenofos)

phosphorothiolothionic acid,
O-ethyl-O-[4-(methylthio)-phenyl]-S-n-propyl ester
(sulprofos).

5

Additional insecticides are listed hereafter by their common
names: triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb,
acephate, azinphosmethyl, chlorpyrifos, dimethoate, fonophos,
isofenphos, methidathion, methamidophos, monocrotophos, phosmet,
10 phosphamidon, phosalone, pirimicarb, phorate, terbufos, trichlorfon,
methoxychlor, bifenthrin, biphenate, cyfluthrin, fenpropathrin,
fluvalinate, flucythrinate, tralomethrin, metal- dehyde and rotenone.

Fungicides:

- 15 methyl 2-benzimidazolecarbamate (carbendazim)
tetramethylthiuram disulfide (thiuram)
n-dodecylguanidine acetate (dodine)
manganese ethylenebisdithiocarbamate (maneb)
1,4-dichloro-2,5-dimethoxybenzene (chloroneb)
20 methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate
(benomyl)
1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-
ylmethyl]-1H-1,2,4-triazole (propiconazole)
2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide
25 (cymoxanil).
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1- yl)-2-butanone
(triadimefon)
N-(trichloromethylthio)tetrahydrophthalimide (captan)
N-(trichloromethylthio)phthalimide (folpet)
30 1-[[[bis(4-fluorophenyl)][methyl]silyl]methyl]-1H-
1,2,4-triazole.

Nematocides:

- S-methyl-1-(dimethylcarbamoyl)-N-(methylcarbamoyloxy)-
35 thioformimidate

S-methyl 1-carbamoyl-N-(methylcarbamoyloxy)thio-
formimidate N-isopropylphosphoramidic acid
O-ethyl O'-[4-(methylthio)-m-tolyl]diester (fenamiphos)

5

Bactericides:

tribasic copper sulfate
streptomycin sulfate

10 Acaricides:

senecioic acid, ester with 2-sec-butyl-4,6-dinitro-
phenol (binapacryl)
6-methyl-1,3-cithiolo[4,5- β]quinoxalin-2-one
(oxythioquinox)

15 ethyl 4,4'-dichlorobenzilate (chlorobenzilate)

1,1-bis(p-chlorophenyl)-2,2,2-trichloroethanol
(dicofol)

bis(pentachloro-2,4-cyclopentadien-1-yl) (dienochlor)
tricyclohexyltin hydroxide (cyhexatin)

20 trans-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-
thiazolidine-3-carboxamide (hexythiazox)

amitraz

propargite

fenbutatin-oxide

25

Biological

Bacillus thuringiensis

Avermectin B.

30 Utility

The compounds of this invention exhibit activity in agricultural
and non-agricultural environments against a wide spectrum of foliar and
soil-inhabiting arthropods which are pests of growing and stored
agronomic crops, forestry, greenhouse crops, ornamentals, nursery crops,
35 stored food and fiber products, livestock, household, and public and

animal health. The compounds are particularly useful against planthoppers and leafhoppers. Those skilled in the art will recognize that not all compounds are equally effective against all pests but the
5 compounds of this invention display activity against:

Larvae of the order Lepidoptera including fall and beet armyworm and other Spodoptera spp., tobacco budworm, corn earworm and other Heliothis spp., European corn borer, navel orangeworm, stalk/stem borers and other pyralids, cabbage and soybean loopers and other loopers,
10 codling moth, grape berry moth and other tortricids, black cutworm, spotted cutworm, other cutworms and other noctuids, diamondback moth, green cloverworm, velvetbean caterpillar, green cloverworm, pink bollworm, gypsy moth, and spruce budworm;

Foliar feeding larvae and adults of the order Coleoptera including
15 Colorado potato beetle, Mexican bean beetle, flea beetle, Japanese beetles, boll weevil, leaf beetles including rice beetle, and root-feeding insects such as the rice water and rice root weevils, Diabrotica spp., Japanese beetle, European chafer and other coleopteran grubs and wireworms;

20 Adults and nymphs of the orders Hemiptera and Homoptera including brown planthopper, small brown planthopper, green leafhopper and other rice plant and leafhoppers, other leafhoppers (Cicadellidae) and planthoppers (Superfamily Fulgoroidea especially Cixiidae, Delphacidae, Flatidae, Fulgoridae, Issidae and Meenoplidae), tarnished
25 plant bugs (Miridae), stink bugs (Pentatomidae), cinch, rice and other seed bugs (Lygaeidae), squash bugs (Coreidae), rice bugs (Alydidae), red bugs and cotton stainers (Pyrrhocoridae), aphids (Aphididae), scales (Coccidae and Diaspididae), lace bugs (Tingidae), cicadas (Cicadidae), spittlebugs (Cercopidae), whiteflies (Aleurodidae), psyllids (Psyllidae),
30 phylloxerans (Phylloxeridae) and mealybugs (Pseudococcidae);

Adults and nymphs of the order Thripidae;

Adults, larvae and eggs of the order acari (mites) including European red mite, two spotted spider mite, rust mites, McDaniel mite, and foliar feed mites;

Adults and immatures of the order Orthoptera including grasshoppers;

Adults and immatures of the order Diptera including leafminers, midges, fruit flies (tephritidae), and soil maggots;

Adults and immatures of the order Thysanoptera including onion thrips and other foliar feeding thrips;

Insect pests of the order Hymenoptera including carpenter ants, bees, hornets and wasps;

Insect pests of the order Diptera including house flies, stable flies, face flies, horn flies, blow flies, and other muscoid fly pests, horse flies, deer flies and other Brachycera, mosquitoes, black flies, biting midges, sand flies, sciarids, and other Nematocera;

Insect pests of the order Orthoptera including cockroaches and crickets;

Insect pests of the order Isoptera including the Eastern subterranean termite and other termites;

Insect pests of the order Mallophaga and Anoplura including the head louse, body louse, chicken head louse and other sucking and chewing parasitic lice that attack man and animals; and

Insect pests of the order Siphonoptera including the cat flea, dog flea and other fleas.

A more preferred spectrum of activity for the compounds of this invention are foliar and soil-inhabiting arthropods which are pests of agronomic crops, as well as greenhouse, ornamental, nursery and fruit crops. The compounds of this invention display activity against economically important agronomic, greenhouse, ornamental, fruit and nursery crop pests.

The specific species for which control is exemplified are: aster leafhopper (Macrosteles fascifrons), rice planthopper (Sogatodes orzicola), black bean aphid (Aphis fabae), and southern corn rootworm (Diabrotica undecimpunctata). The pest control protection afforded by compounds of the present invention is not limited, however, to these species.

Application

Arthropod pests are controlled by applying one or more of the Formula I compounds of this invention, in an effective amount, to the locus of infestation, to the area to be protected, or directly on the pests to be controlled. Because of the diversity of habitat and behavior of these arthropod pest species, many different methods of application are employed. A preferred method of application is by spraying with equipment that directs the compound to the environment of the pests, on the foliage, in the soil or paddy, to the plant part that is infested or needs to be protected. Alternatively, granular formulations of these compounds can be applied to or incorporated into the soil, paddy or nursery box. Other methods of application can also be employed including direct and residual sprays.

The compounds of this invention can be applied in their pure state, but most often application will be of a formulation comprising one or more compounds in a carrier that may include diluents and/or surfactants in a formulation compatible with agronomic and nonagronomic utility. Preferred methods of application involve spraying a water dispersion, refined oil solution or dust containing the compound.

The rate of application of the Formula I compounds required for effective control will depend on such factors and the species of arthropod to be controlled, the pest's life cycle, life stage, location, time of year, host crop, feeding and mating behavior, ambient moisture and temperature, and the like. In general, application rates of 0.55-0.055 kg of active ingredient per hectare are sufficient to provide large-scale effective control of pests in agronomic ecosystems under normal circumstances. Application rates as low as about 0.1 mg/sq meter or less up to about 150 mg/sq meter or more can be employed on arthropods in a nonagronomic environment such as the household or other building or nonagronomic locus.

The following Examples demonstrate the control efficacy of compounds of Formula I on specific pests; See Table 1 for compound descriptions. Compounds not listed with data were either not screened

on that test species or produced less than 80% mortality when tested as described in Examples 3 and 4.

EXAMPLE 3

5 Aster Leafhopper

Test units were prepared from a series of 12 oz. (350 ml) cups, each containing oat (Avena satavia) seedlings in a 1-inch layer of sterilized soil. Solutions of test compounds were prepared in a 75 acetone:25 water solvent and applied to the seedlings with a hydraulic sprayer by passing
10 three sets of cups on a conveyor belt, beneath a flat-fan nozzle calibrated to deliver 0.055 kg/HA at 30 psi (207 kPa). Approximately 1 hour after treatment, a thin layer of sand was placed over the soil in each cup, the units capped and 10-20 adult aster leafhoppers (Macrostelus fascifrons) each aspirated into the cups. The units were held at 27°C, 50% RH and
15 14L:10D for 48 hours, after which time mortality readings were taken. The following table lists the activity of the compounds against aster leafhopper.

EXAMPLE 4

20 Rice Planthopper

The test procedure of Example 3 was repeated for efficacy against adults of the rice planthopper (Sogatodes orzicola) except four sets of cups containing rice (Oryza satavia) seedlings were treated. The sprayer was calibrated to deliver 0.055 kg/HA. The results are tabulated below.

25

TABLE

| <u>Compound</u> | <u>% Mortality Leafhopper</u> | <u>% Mortality Planthopper</u> |
|-----------------|-----------------------------------|------------------------------------|
| 1 | 100 | <80 |
| 2 | 100 | 100 |
| 14 | 100 | 100 |
| 15 | 98 | 82 |

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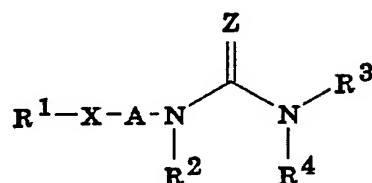
CLAIMS

What is claimed is:

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1. An arthropodicial composition comprising, as active ingredient, a compound of the formula:

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in an amount effective to control planthoppers and leafhoppers, and a carrier therefor, wherein:

Z is selected from the group CHNO_2 and NNO_2 ;

X is selected from S(O)_n ;

20

A is selected from the group $\text{C}_1\text{-C}_4$ alkylene optionally substituted with $\text{C}_1\text{-C}_3$ alkyl, $\text{C}_2\text{-C}_3$ alkoxy carbonyl, halogen and CN;

R^1 is selected from the group $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ haloalkyl, $\text{C}_3\text{-C}_6$ cycloalkyl and $\text{C}_4\text{-C}_6$ cycloalkylalkyl;

25

n is 0, 1 or 2;

R^2 and R^3 are independently selected from the group H, CH_2CN , $\text{C}_1\text{-C}_4$ alkyl, CHO, $\text{C}_2\text{-C}_4$ alkylcarbonyl, $\text{C}_2\text{-C}_3$ alkoxy carbonyl, $\text{C}_2\text{-C}_4$ alkoxyalkyl, $\text{C}_3\text{-C}_6$ dialkoxyalkyl, $\text{C}_1\text{-C}_3$ alkoxy, $\text{C}_1\text{-C}_3$ alkylsulfonyl, $\text{C}_3\text{-C}_4$ alkenyl, $\text{C}_3\text{-C}_4$ alkynyl, $\text{C}_1\text{-C}_4$ alkylamino, $\text{C}_2\text{-C}_4$ dialkylamino and benzyl substituted with R^5 ;

30

R^4 is selected from the group $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ haloalkyl, $\text{C}_3\text{-C}_6$ cycloalkyl and $\text{C}_4\text{-C}_6$ cycloalkylalkyl; or

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R² and R⁴ can be taken together as C₂-C₃ alkylene or C₂-C₃ alkenylene each optionally substituted with 1-4 C₁-C₂ alkyl; and

5 R⁵ is selected from the group halogen, C₁-C₂ alkyl, C₁-C₂ haloalkyl, C₁-C₂ alkoxy, C₁-C₂ thioalkyl, C₁-C₂ halothioalkyl, C₁-C₂ haloalkoxy, NO₂ and CN.

2. A composition according to Claim 1 wherein Z is CHNO_2 .

3. A composition according to Claim 1 wherein Z is NNO_2 .

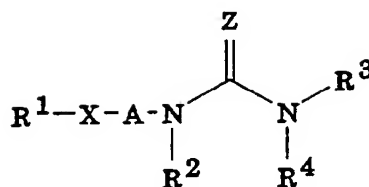
4. A composition according to Claim 2 wherein:
A is CH_2CH_2 ;
 R^1 is selected from the group $\text{C}_1\text{-C}_4$ alkyl;
 R^2 and R^3 are independently selected from the group H,
 $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_2\text{-C}_3$ alkoxy carbonyl and $\text{C}_2\text{-C}_4$
alkyl carbonyl; and
 R^4 is selected from the group $\text{C}_1\text{-C}_4$ alkyl.

5. A composition according to Claim 2 wherein R² and R⁴ are taken together and independently selected from the group C₂-C₃ alkylene and C₂-C₃ alkenylene, each optionally substituted by 1-4 C₁-C₄ alkyl.

6. A composition according to Claim 4 wherein X is S.

7. A composition according to Claim 5 wherein X is S.

8. A method for controlling planthoppers and leafhoppers which comprises applying to them or to their environment an effective amount of a compound of the formula:



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wherein:

- 10 Z is selected from the group CHNO_2 and NNO_2 ;
 X is selected from S(O)_n ;
 A is selected from the group $\text{C}_1\text{-C}_4$ alkylene optionally
 substituted with $\text{C}_1\text{-C}_3$ alkyl, $\text{C}_2\text{-C}_3$ alkoxy carbonyl, halogen
 and CN;
 15 R^1 is selected from the group $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ haloalkyl,
 $\text{C}_3\text{-C}_6$ cycloalkyl and $\text{C}_4\text{-C}_6$ cycloalkylalkyl;
 n is 0, 1 or 2;
 R^2 and R^3 are independently selected from the group H, CH_2CN ,
 $\text{C}_1\text{-C}_4$ alkyl, CHO, $\text{C}_2\text{-C}_4$ alkylcarbonyl, $\text{C}_2\text{-C}_3$
 20 alkoxy carbonyl $\text{C}_2\text{-C}_4$ alkoxyalkyl, $\text{C}_3\text{-C}_6$ dialkoxyalkyl,
 $\text{C}_1\text{-C}_3$ alkoxy, $\text{C}_1\text{-C}_3$ alkylsulfonyl, $\text{C}_3\text{-C}_4$ alkenyl, $\text{C}_3\text{-C}_4$
 alkynyl, $\text{C}_1\text{-C}_4$ alkylamino, $\text{C}_2\text{-C}_4$ dialkylamino and benzyl
 substituted with R^5 ;
 R^4 is selected from the group $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ haloalkyl,
 $\text{C}_3\text{-C}_6$ cycloalkyl and $\text{C}_4\text{-C}_6$ cycloalkylalkyl; or
 R^2 and R^4 can be taken together as $\text{C}_2\text{-C}_3$ alkylene or $\text{C}_2\text{-C}_3$
 alkenylene each optionally substituted with 1-4 $\text{C}_1\text{-C}_2$ alkyl;
 and
 30 R^5 is selected from the group halogen, $\text{C}_1\text{-C}_2$ alkyl, $\text{C}_1\text{-C}_2$
 haloalkyl, $\text{C}_1\text{-C}_2$ alkoxy, $\text{C}_1\text{-C}_2$ thioalkyl, $\text{C}_1\text{-C}_2$
 haloalkoxy, $\text{C}_1\text{-C}_2$ haloalkoxy, NO_2 and CN.

9. A method according to Claim 8 wherein Z is CHNO_2 .

10. A method according to Claim 8 wherein Z is NNO_2 .

11. A method according to Claim 9 wherein:

5

A is CH_2CH_2 ;

R^1 is selected from the group $\text{C}_1\text{-C}_4$ alkyl;

R^2 and R^3 are independently selected from the group H,
 $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_2\text{-C}_3$ alkoxy carbonyl and $\text{C}_2\text{-C}_4$

alkyl carbonyl; and

10

R^4 is selected from the group $\text{C}_1\text{-C}_4$ alkyl.

12. A method according to Claim 9 wherein R^2 and R^4 are taken
together and independently selected from the group $\text{C}_2\text{-C}_3$ alkylene and
 $\text{C}_2\text{-C}_3$ alkenylene, each optionally substituted by 1-4 $\text{C}_1\text{-C}_4$ alkyl.

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13. A method according to Claim 11 wherein X is S.

14. A method according to Claim 12 wherein X is S.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/03118

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5 A 01 N 35/08 A 01 N 43/50 A 01 N 43/54
A 01 N 51/00

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl.5

A 01 N

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
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| X | FR,A,2322849 (SHELL) 1 April 1977, see claims 2,5 & US-A-4 025 529 (cited in the application) --- | 1,2,4-9 ,11-14 |
| X | EP,A,0302389 (TAKEDA CHEMICAL INDUSTRIES) 8 February 1989, see claim 12, page 3, line 5 - page 5, line 39; page 42, line 31 (cited in the application) --- | 1,2,8,9 |
| X,P | EP,A,0381130 (TAKEDA CHEMICAL INDUSTRIES) 8 August 1990, see page 5, formula V; page 6, lines 13-18; page 20, lines 1-3 --- -/- | 1,2,8,9 |

¹⁰ Special categories of cited documents:

"A" document defining the general state of the art which is not
considered to be of particular relevance

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filing date

"L" document which may throw doubts on priority claim(s) or
which is cited to establish the publication date of another
citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or
other means

"P" document published prior to the international filing date but
later than the priority date claimed

"T" later document published after the international filing date
or priority date and not in conflict with the application but
cited to understand the principle or theory underlying the
invention

"X" document of particular relevance; the claimed invention
cannot be considered novel or cannot be considered to
involve an inventive step

"Y" document of particular relevance; the claimed invention
cannot be considered to involve an inventive step when the
document is combined with one or more other such docu-
ments, such combination being obvious to a person skilled
in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

27-08-1991

Date of Mailing of this International Search Report

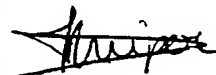
04 OCT 1991

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

Mme N. KUIPER



| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) | | |
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| A | <p>EP,A,0254859 (NIHON TOKUSHU NOYAKU SEIZO) 3 February 1988, & US-A-4 806 553 (cited in the application)</p> <p>-----</p> | |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9103118

SA 47604

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 19/09/91
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